Supplementary Information to:

"Effects of surface curvature and surface chemistry on the structure and activity of proteins adsorbed in nanopores"

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Materials and equipment

Hydrochloric acid (ACS reagent, 37 wt.%), tetraethyl orthosilicate, (reagent grade, 98%), tri-block copolymer poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, molecular weight = 5,800 g mol^{-1}, $EO_{20}PO_{70}EO_{20}$), trimethoxy(propyl)silane (Aldrich, 98%), toluene (anhydrous, 99.8%), and 2-propanol (anhydrous, 99.5%) were all purchased from Sigma-Aldrich. Field-emission scanning electron microscopy images (FESEM) were taken using a Hitachi S-4800 microscope. Small-angle X-ray scattering (SAXS) patterns were obtained using a Bruker Nanostar small-angle X-ray scattering machine. Nitrogen adsorption and desorption isotherms were measured using a Quantachrome Autosorb 1C sorption analyzer.

Synthesis of mesoporous silica SBA-15 and propyl-functionalized SBA-15

Mesoporous SBA-15 with different pore sizes was synthesized as follows. In general, 120 g of 2M HCl solution was added to a P123 solution containing 4g of block-copolymer P123 and 30 g of deionized water. The mixture was stirred for 2 hours at 40 °C. Then, 9 g of tetraethyl orthosilicate was slowly dropped into the homogeneous solution, while it was rapidly stirred for 10 minutes. The sample mixture was then kept static for 24 hours. After this, the sample was transferred to an oven at a desired temperature T for hydrothermal aging. The differences in pore size of mesoporous SBA-15 were achieved by hydrothermal aging of the silica/surfactant nanocomposites at different temperatures (T) for 48 hours (T = 40 °C to 150 °C). The solid product was filtered, washed several times with deionized water, and dried overnight in the oven at 100 °C. The final product was recovered by calcining silica/polymer composites at 540 °C for 24 hours. Samples synthesized at a temperature T (°C) are denoted by SBA-15_T, e.g. SBA-15_40 for T = 40 °C. Using this procedure, by simply changing the hydrothermal aging temperature, monodisperse particles (that is, with a very narrow particle size distribution) with a rod-like morphology are formed.

Some of the SBA-15_T samples were functionalized with propyl groups, leading to C_3SBA-15_T. Functionalization occurred by post-synthesis grafting of propyl silane moieties on the surface of the nanopores. Generally, 1 g of SBA-15 was suspended in 30 mL of toluene in a double-necked 100-mL round-bottomed flask. A reflux condenser was fitted at one end and a rubber septum closed the flask at the other end. Around 0.3 mL of deionized water was added to the suspension. At this point, the silica immediately aggregated. The mixture was stirred for at least 2 hours at room temperature to disperse the particles and to let a stoichiometric quantity of water distribute throughout the pore network. After this, 1.5 mL of trimethoxy (propyl) silane was injected into the mixture, which was stirred for 6 hours to homogeneously distribute the functionalizing agent. The mixture was then heated and refluxed for another 6 hours at a temperature of 105 °C. During the reaction process, the mixture turned from milky white to a light brown color. The reaction mixture was then cooled down to room temperature. Solid product was filtered out and washed several times with 2-propanol. The wet product was dried under vacuum at room temperature for three days. The solid product was collected for characterization. By following this procedure, propyl-functionalized SBA-15 (C_3SBA-15) with a monolayer of propyl-groups was synthesized. This material has a hydrophobic surface.

Textural properties of SBA-15 and C_3SBA-15

All SBA-15 and C_3SBA-15 particles show a rod-like morphology and low polydispersity (**Fig. S1 to S3**). The SAXS patterns (**Fig. S4A and B**) reveal at least three well-resolved Bragg diffraction peaks, which can be indexed as (100), (110), and (200). These peaks are associated with the *p6mm* 2D hexagonal periodicity of the cylindrical pore array in the SBA-15 and C_3SBA-15 samples. The clear (110) and (200) peaks indicate long-range hexagonal order of the nanopores. The position of the (100) peak shifts to a lower angle with increasing temperature of the hydrothermal treatment. This corresponds to an increased size of the unit cell under different synthesis conditions. N_2 adsorption and desorption isotherms of SBA-15 and C_3SBA-15 (**Fig. S5A and B**) contain a hysteresis loop defined as of type H1 according to the IUPAC classification, which is associated with porous materials containing well-defined cylindrical pore channels. All samples have capillary condensation steps at a relative pressure (to atmospheric), P/P_0, between 0.5~0.6 for synthesis at a low aging temperature, and shift to a higher relative pressure between 0.7~0.8 for synthesis at a high aging temperature. The clear shift to the right of the capillary condensation and hysteresis steps with increased aging temperatures indicates an increased pore size. This matches the increased unit cell

size seen in the SAXS patterns. A well-controlled nanopore diameter and a narrow pore size distribution for each sample, as calculated from the NLDFT method, can be seen in Figures S5A and B (inserts). The steep nitrogen hysteresis and condensation steps of C_3SBA-15 for all different pore diameters also suggest that the functional moieties indeed form monolayers with a high surface coverage on the nanopore surface (**Fig. S5B**).

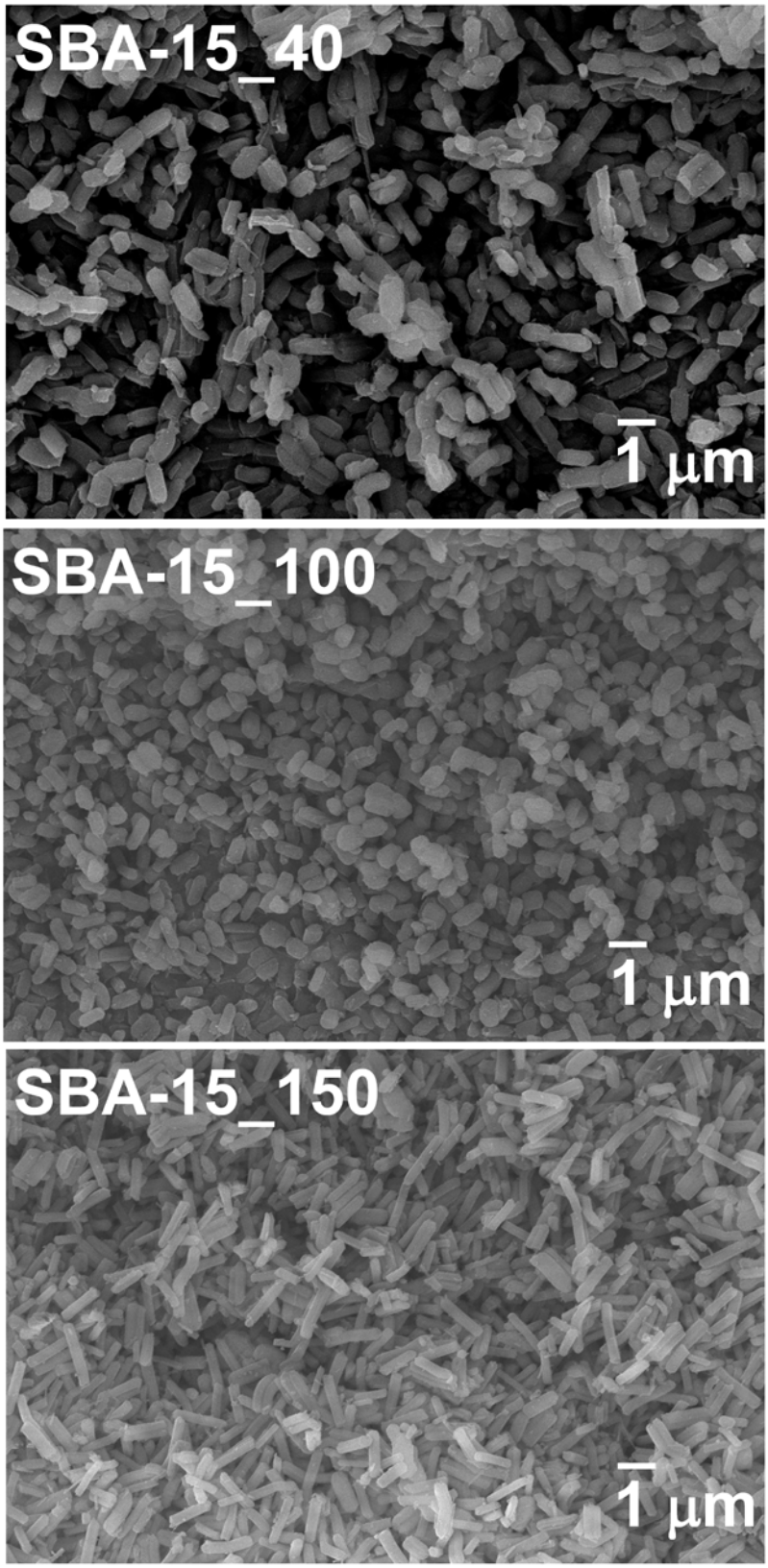

Figure S1. FESEM images of SBA-15 synthesized at different hydrothermal aging temperatures.

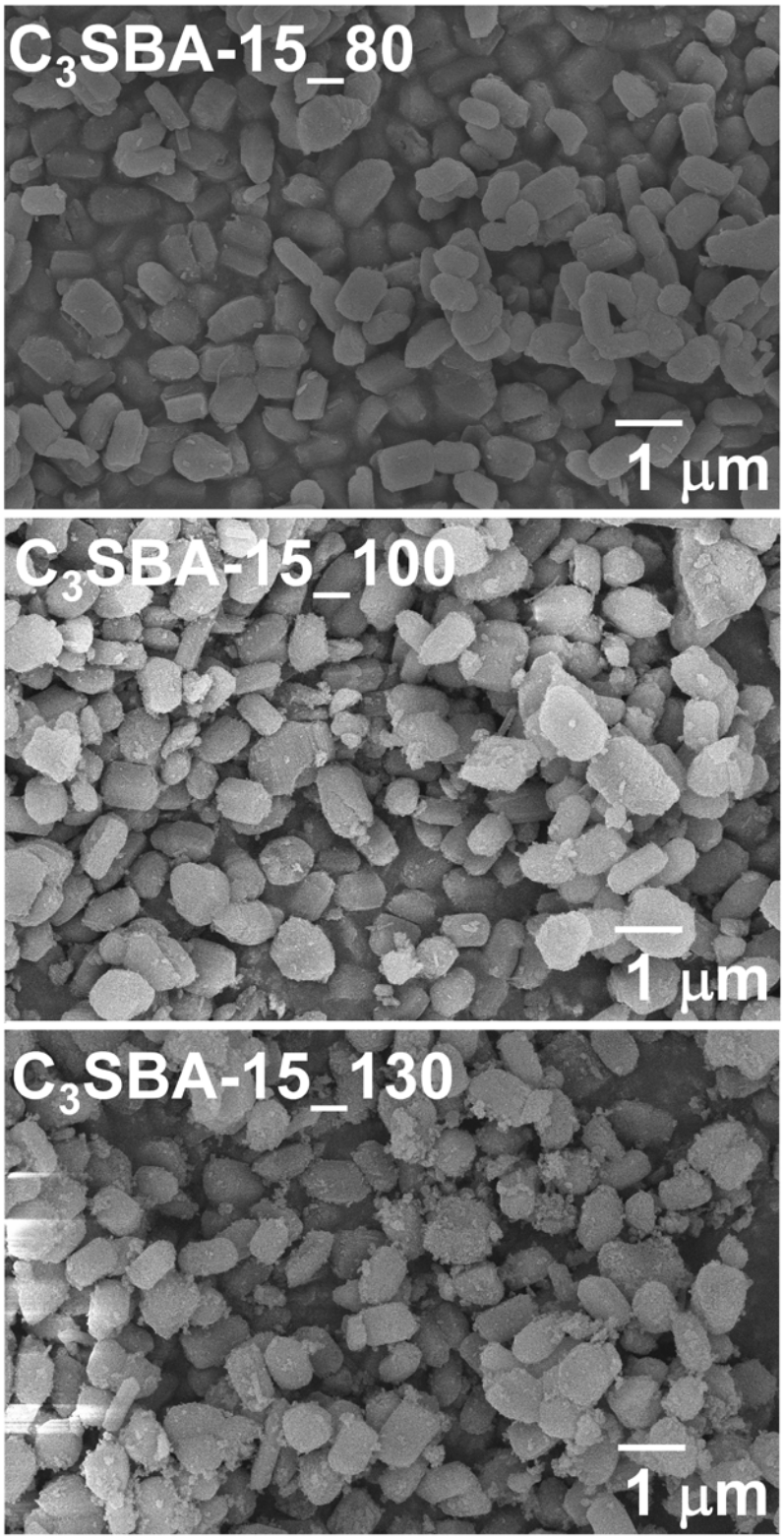

Figure S2. FESEM images of propyl-functionalized SBA-15 (C_3SBA-15) synthesized using different SBA-15 templates.

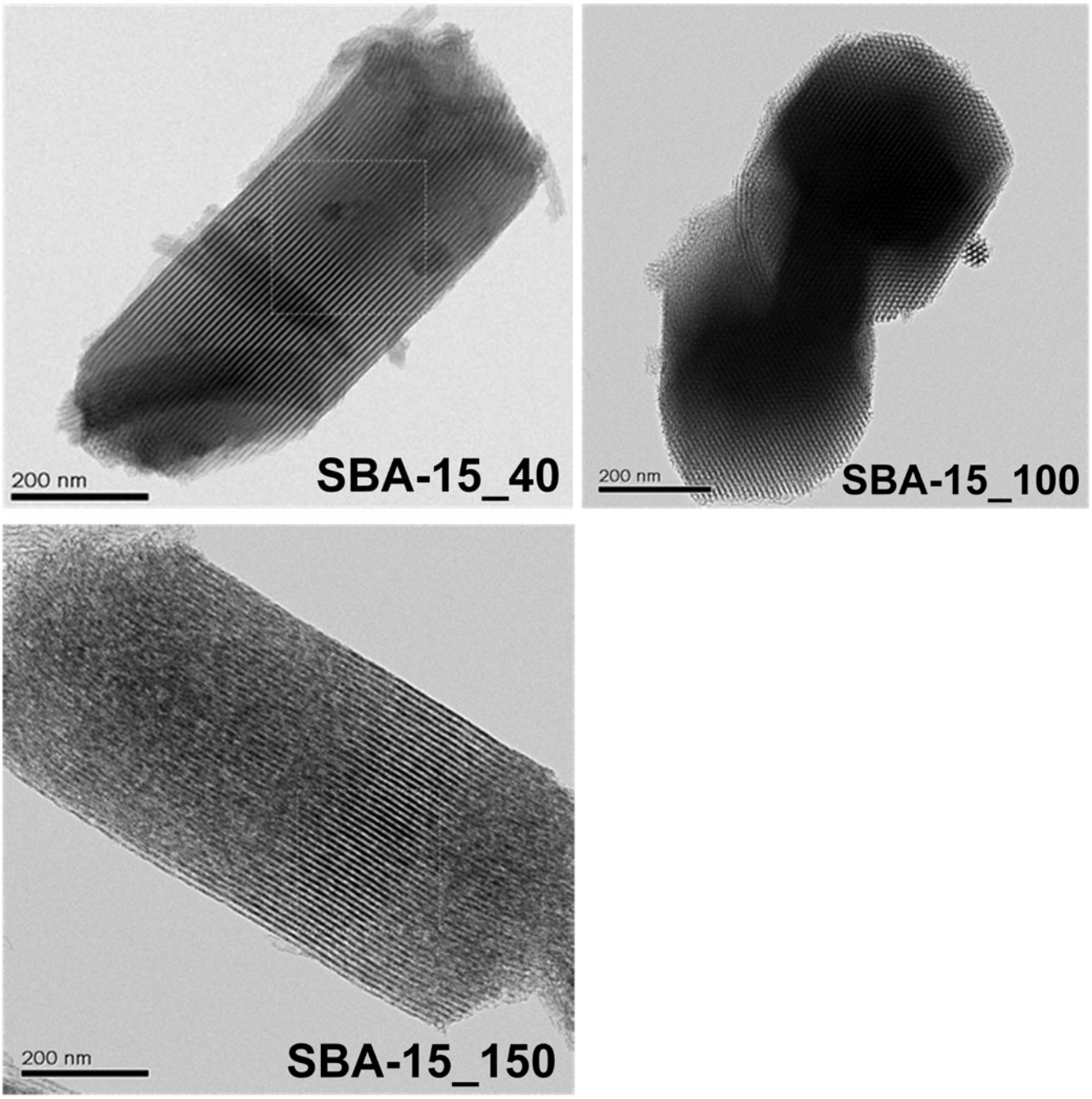

Figure S3. HRTEM images of SBA-15 synthesized at different hydrothermal aging temperatures.

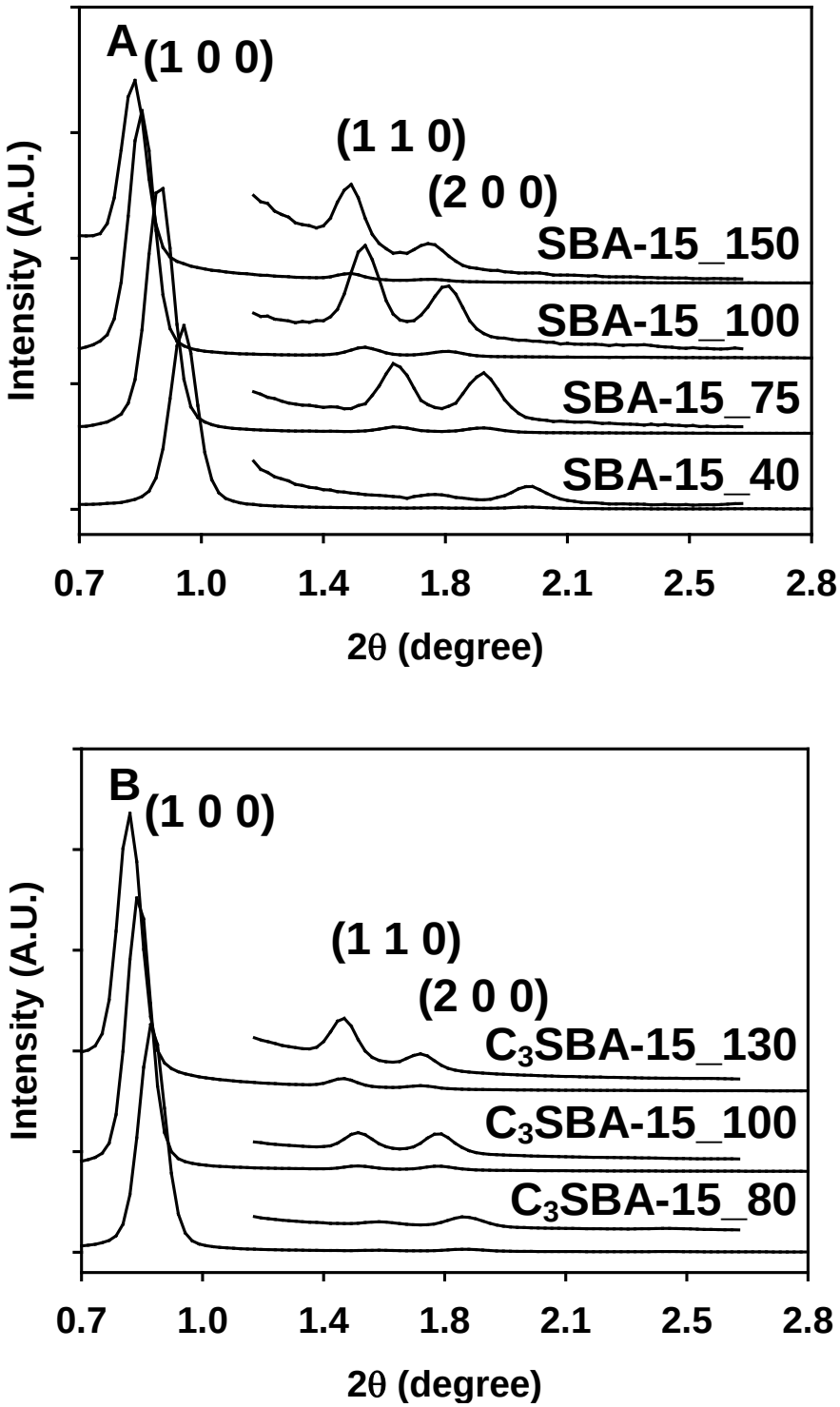

Figure S4. SAXS patterns of SBA-15 (A) and C_3SBA-15 (B), aged at different temperatures T (SBA-15_T, C_3SBA-15_T).

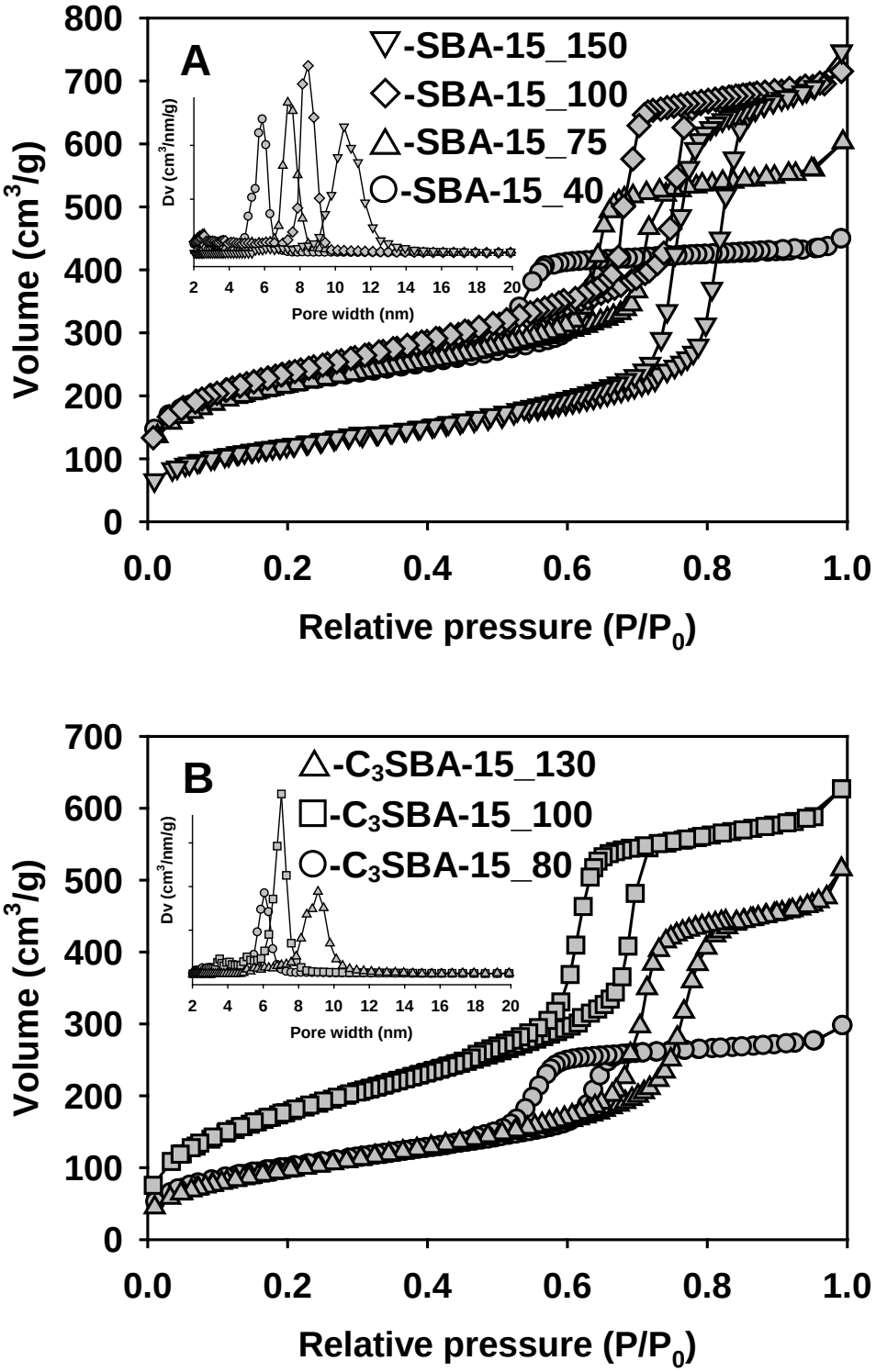

Figure S5. N_2 adsorption/desorption isotherms and NLDFT pore size distribution (inserts) of SBA-15 (A) and C_3SBA-15 (B), aged at different temperatures T (SBA-15_T, C_3SBA-15_T).