Supporting Information:

Hierarchically Ordered Macro-/mesoporous Silica Monolith: Tuning the Macropore Entrance Size for Size-Selective Adsorption of Protein

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Preparation of poly(St-co-TMSPM) Colloidal Crystals

Monodisperse poly(St-co-TMSPM) (donated as PST) microspheres with a mean size of ~ 1.2 μm were prepared through a dispersion polymerization approach.[31] For a typical preparation, 10 g of styrene, 8.0 g of PVP, 2.5 g of TMSPM and 0.2 g of 2,2-azobisiso-butyronitrile (AIBN) were dissolved in a mixture of ethanol (140 mL) and H_2O (10 mL). The obtained solution was then added into a 250 mL four-neck round bottom flask equipped with a mechanical stirrer, a refluxing condenser, and a nitrogen inlet. After sealing in a nitrogen atmosphere, the reactor was submerged in a water bath and the polymerization was carried out with a stirring speed of 100 rpm at 70 °C for 24 h.

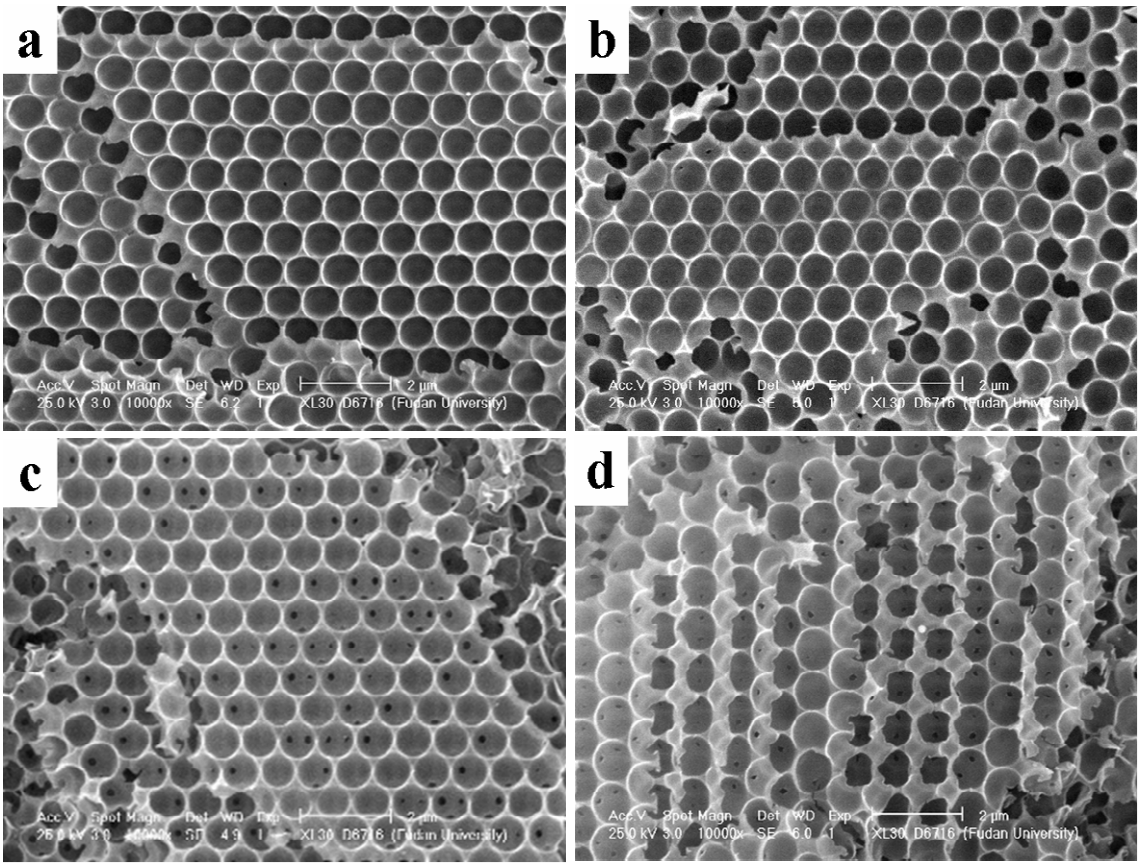

Figure S1. SEM images of the samples (a) HOPS-80-12h, (b) HOPS-80-24h, (c) HOPS-90-12h and (d) HOPS-90-24h synthesized by using poly-(St-*co*-TMSPM) colloidal microspheres as a template sintered at different temperatures and times (a) 80 °C for 12 h, (b) 80 °C for 24 h, (c) 90 °C for 12 h and (d) 90 °C for 24 h.

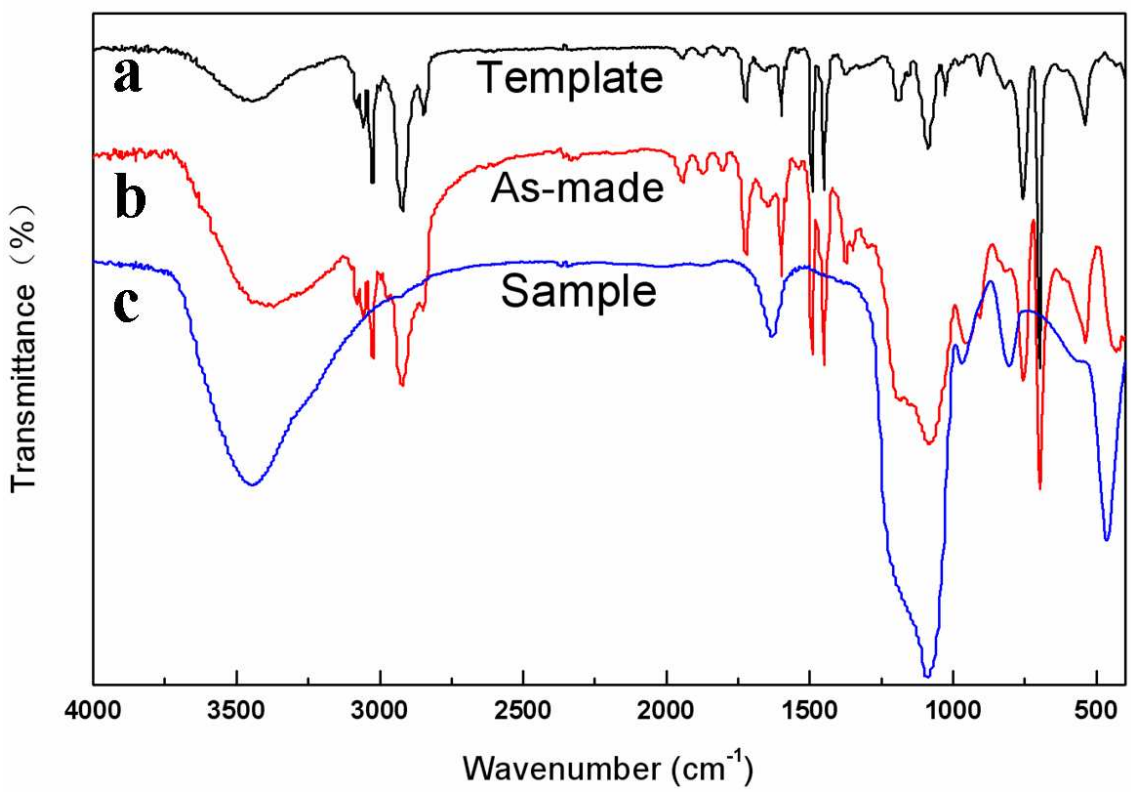

Figure S2. The FT-IR spectra of (a) the poly(St-*co*-TMSPM) colloidal microsphere templates, (b) the impregnated poly(St-co-TMSPM) colloidal microsphere templates and (c) the hierarchically ordered porous silica (HOPS-01-01) after the calcination.

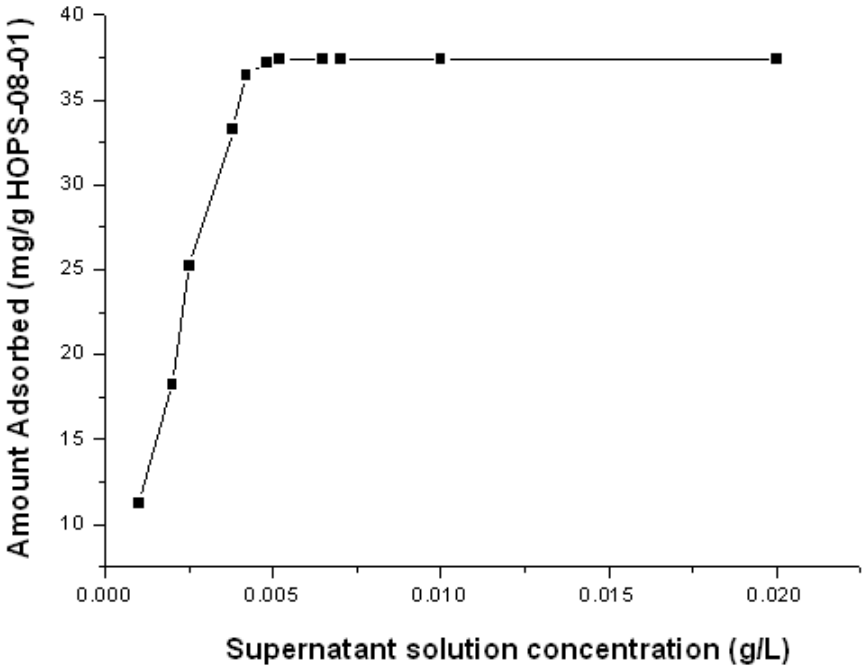

Figure S3. The adsorption isotherm of Cyt. c at room temperature using HOPS-08-10 sample. The solutions of Cyt.c were prepared in NaOH/$NaHCO_3$ buffer solution (pH = 9.5).

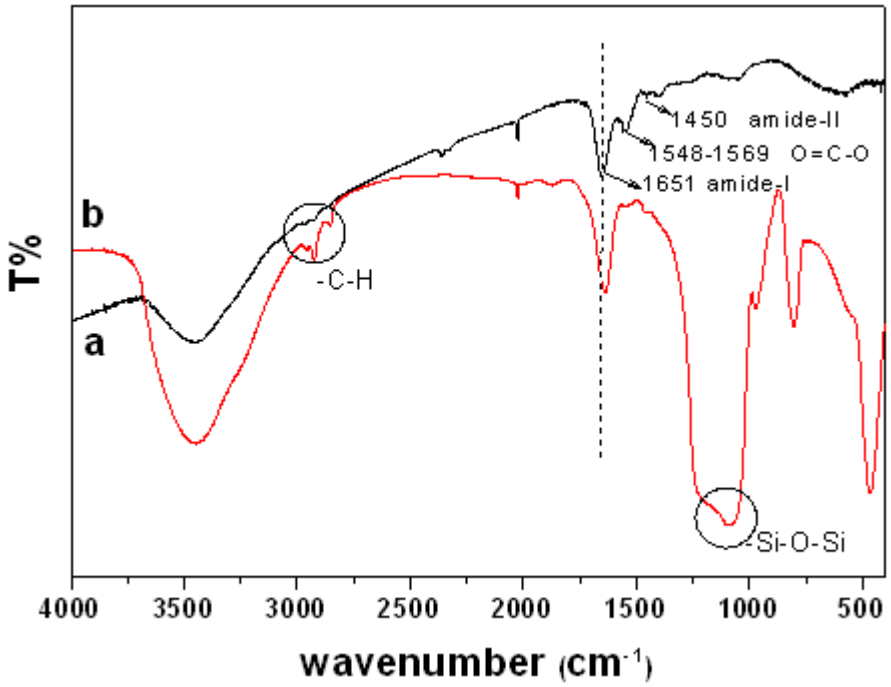

Figure S4. FT-IR spectra of Cyt. c (a) before and (b) after adsorbed on HOPS-08-01 sample, wherein, the absorption bands at 1651and 1450 cm^{-1} are attributed to the amide-I and amide-II of Cyt.c molecules, respectively, and the bands at 1548 – 1569 cm^{-1} are due the carboxylate group. The peaks at around 2900 cm^{-1} are from the C-H stretching of Cyt.c molecules. All these peaks are present in both samples except for the intensity difference due the presence of HOPS silica material.