Electronic Supplementary Material (ESI) for Nanoscale
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Supporting Information for "Synthesis of Hierarchically Nanoporous Silica Films for Controlled Drug Loading and Release"

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EXPERIMENTAL SECTION

Materials: Triblock copolymer Pluronic F127 (PEO_{106}-PPO_{70}-PEO_{106}) was purchased from Sigma. Tetraethylorthosilicate (TEOS, Shanghai Normal Co.) served as silica precursor, and HCl (37%, Shanghai Normal Co.) was used to catalyze the condensation of TEOS. Rhodamine B (Sigma) was designated as rhodamine in this paper for simplicity. Ampicillin was purchased from a local drugstore. Beef extract, peptone, NaCl, and agarose powder were purchased from Sinopharm Chemical Reagent Co., Ltd. Bacteria culture of *E. coli* was cultivated in a standard media LB for 24 h at temperature 37 °C and pH 7. All the reagents were used without further purification.

Preparation: Polystyrene (PS) spheres were synthesized through emulsion polymerization.[27] The size of the PS spheres can be easily tailored through changing the volume of styrene monomer, which allows fine control over the template structure and consequently the final macroporous structure. A homogeneous and stable aqueous dispersion containing monodisperse PS spheres (0.3%, v/v) was obtained by repeated centrifugation. PS opal films were formed on pre-cleaned glass substrate by a lifting method.[27] The thickness of the polymer spheres assembly can be adjusted by changing the

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suspension concentration and the lifting speed. Spheres were assembled to form a close-packed hexagonal array (**Figure S1**). Finally, the resulting PS opal films were heated at 85°C for 30 min to adhere the spheres tightly to each other. For triblock copolymer assembly, F127 (1 g) and HCl (0.1 g, 2 mol/L) were dissolved in ethanol (12.5 g) and H_2O (0.8 g) at 40 °C. After stirring at room temperature for 2 h, TEOS (2.08 g) was added and then the mixture was continuously stirred at 60 °C for 1 hour. Silica thin films were then fabricated by spin-coating (3000 r.p.m.) the solution into the pre-formed PS opal array. The samples were left to dry under airflow overnight, and were then heated at 2 °C per minute to 450 °C and held at this temperature for 3 h to further condense the inorganic precursor and remove templates. EISA method and slow heating process would contribute to the uniform of the films with a little cracks and defects.

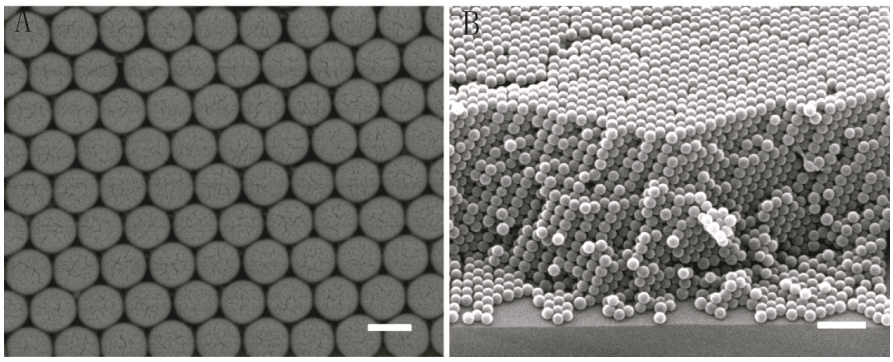

Figure S1. SEM images of the polystyrene array film. A: top-view, the scale bar is 200 nm; B: side-view, the scale bar is 1 μm.

Molecule adsorption and release: Ordered porous films were investigated by adsorption and release of different molecules. Typically, the films to be studied were put in a rhodamine solution (0.1 mM) for a period ranging from 3 to 300 seconds. An agarose solution (0.5%) was prepared in de-ionized water at 70 °C, and then poured over the surface of the silica films (0.2 ml per 1.0 × 1.0 cm^2) to reduce the molecule release rate. After 20 min of gelation at room temperature, the films were dried overnight in air. To investigate the release behavior of these films, the loaded films were incubated in

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de-ionized water (20 mL) with constant shaking at room temperature. At designated time intervals (2^n min), the solution in the beaker was taken out and changed to fresh de-ionized water with same volume (**Figure 3**). All the solutions with released molecules were quantified for fluorescence emission by using a fluorimeter.

E. coli culture: E. coli was grown aerobically in LB broth at 37℃ for culture. Gel medium was made by first adding beef extract (1.5 g), peptone (5.0 g), NaCl (2.5 g) and agarose powder (7.5 g) into distilled water (500 ml). Prior to autoclaving, the medium were adjusted to the pH 7 with sodium hydroxide, and boiled at 90 °C every time before use. The hot medium was quickly poured into culture Petri-dishes. After the gels cooled down to room temperature, these agarose gel medium substrates were used in all subsequent experiments. Take Ampicillin solution (0.1 ml) released at each designated time intervals (2^n min), and mixed with *E. coli* bacterium suspension (0.1 ml, 0.1% v:v). Then these mixtures were uniformly coated on the prepared agarose gel medium substrates by a glass spreader. Finally, all these substrates were put into a cell culture incubator at 37 °C together for 24 hours.