

Electronic Supplementary Information (ESI)

A. Experimental details

1. Preparation of mesoporous silica films:

The precursor solution was firstly prepared by mixing TEOS, 0.1 M HCl solution (0.15 g), THF (2.45 g), PS(20000)-*b*-PEO(6500) block copolymer (0.05 g). After stirring for 1 h, a transparent solution was obtained. To investigate the optimal amount of TEOS, several precursor solutions were prepared by changing the amount of TEOS as follows: 0.5 g (**Solution A**), 0.33 g (**Solution B**), 0.17 g (**Solution C**), 0.08 g (**Solution D**), and 0.04 g (**Solution E**). The weight ratios of TEOS of block copolymer were varied 10 (**Solution A**), 6.6 (**Solution B**), 3.4 (**Solution C**), 1.6 (**Solution D**), and 0.8 (**Solution E**), respectively.

Then, fabrication of thin films was conducted by a dip coater ND-0407-SI (SDI Company., LTD.). Before the use, silicon substrates were washed with ethanol, HF solution, and distilled water. The solutions were dip-coated on the substrates at various speeds (from 1 mm•sec⁻¹ to 20 μm•sec⁻¹). After that, the thin films were dried in air and then calcined at 600 °C for 6 h. The film thickness was around 100 nm.

2. Preparation of a precursor solution for niobia films:

The mixture consisting of niobium ethoxide (0.750 g), acetic acid (0.575 g) and concentrated HCl (0.30 g) was added to 2.5 g of THF solution including PS(20000)-*b*-PEO(6500) (2.0 wt % containing 0.05 g copolymer). After stirring for 1 h, the solution was coated by a dip-coating method. Finally, the as-prepared films were aged at 100 °C for 1 day and calcined at 500 °C and 600 °C for 6 h. When the

as-prepared films were calcined at lower temperature (below 400 °C), mesoporous structures were not clearly confirmed. Because PS-*b*-PEO block polymers generally burn out completely at around 500 °C in air, a part of block copolymers still remained in the films. The film thickness was around 100 nm.

B. Additional characterization data

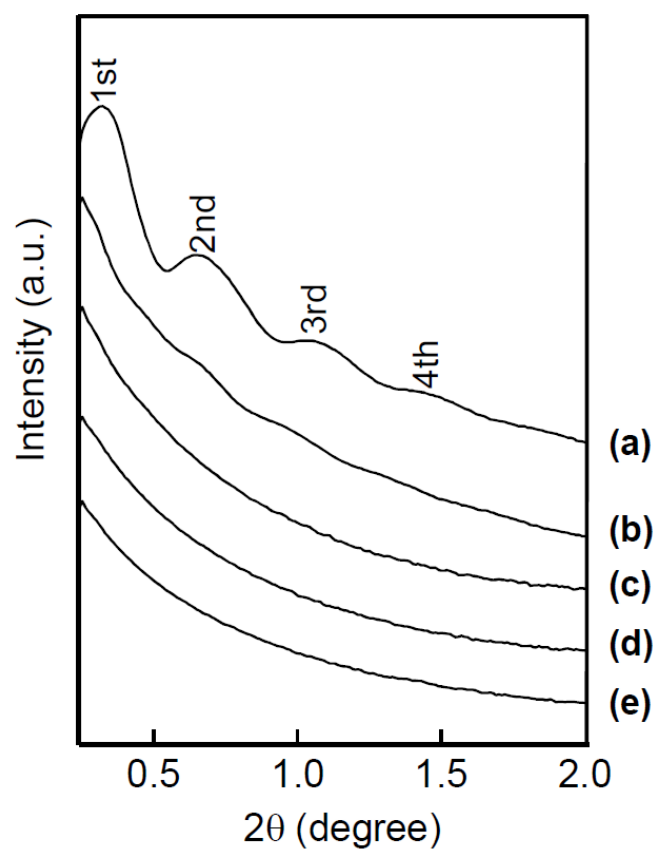


Figure S1 SAXS patterns of mesoporous silica films prepared from (a) **Solution A**, (b) **Solution B**, (c) **Solution C**, (d) **Solution D**, and (e) **Solution E**, respectively. The weight ratios of TEOS of block copolymer are 10 (**Solution A**), 6.6 (**Solution B**), 3.4 (**Solution C**), 1.6 (**Solution D**), and 0.8 (**Solution E**), respectively. The several peaks of pattern (a) are 27.6 nm ($2\theta = 0.32^\circ$), 13.6 nm ($2\theta = 0.65^\circ$), 8.5 nm ($2\theta = 1.04^\circ$), and 6.0 nm ($2\theta = 1.47^\circ$), respectively.

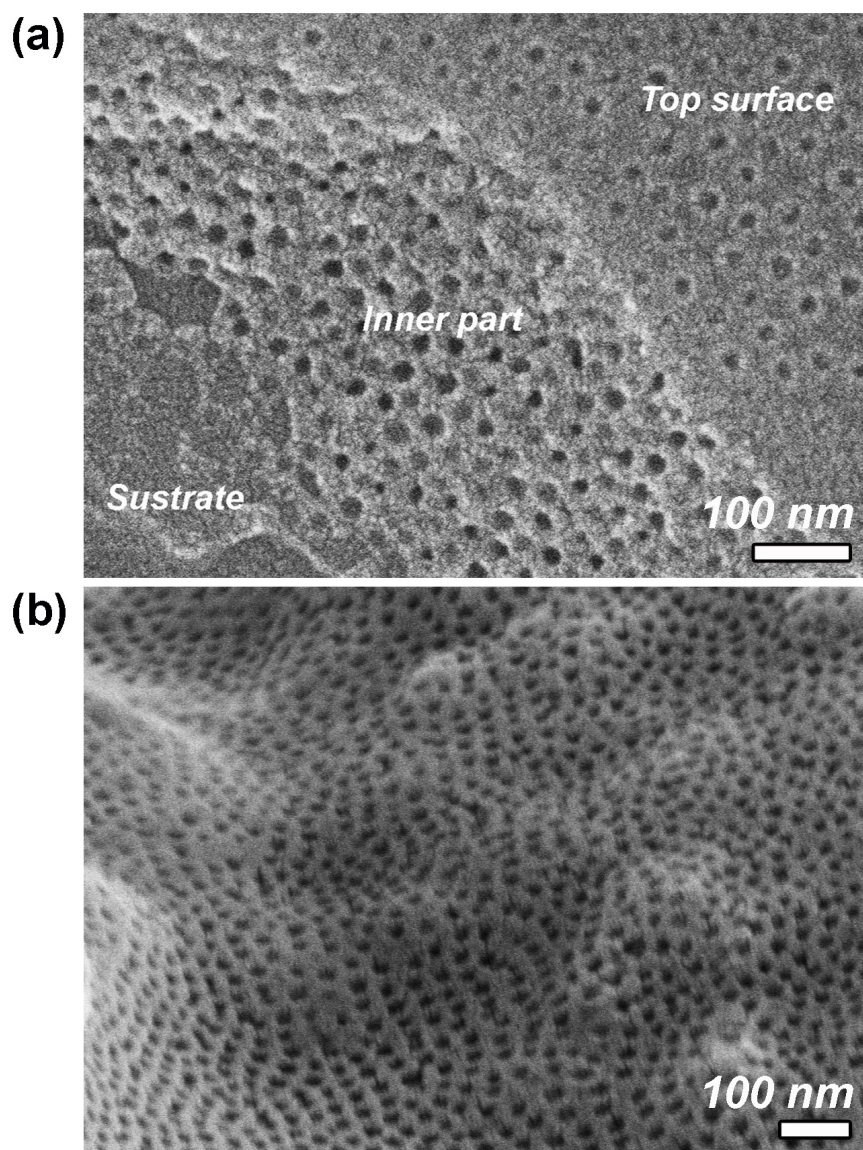


Figure S2 SEM images of the calcined mesoporous silica films prepared under dip-coating speed ($50 \mu\text{m}\cdot\text{sec}^{-1}$). (a) Bird-eye view of the accidentally cracked area. The cross-sectional part shows that lots of mesopores are closely packed from the substrate to the top surface of the film. (b) Top-surface image after the removal of the upper layers of silica film.

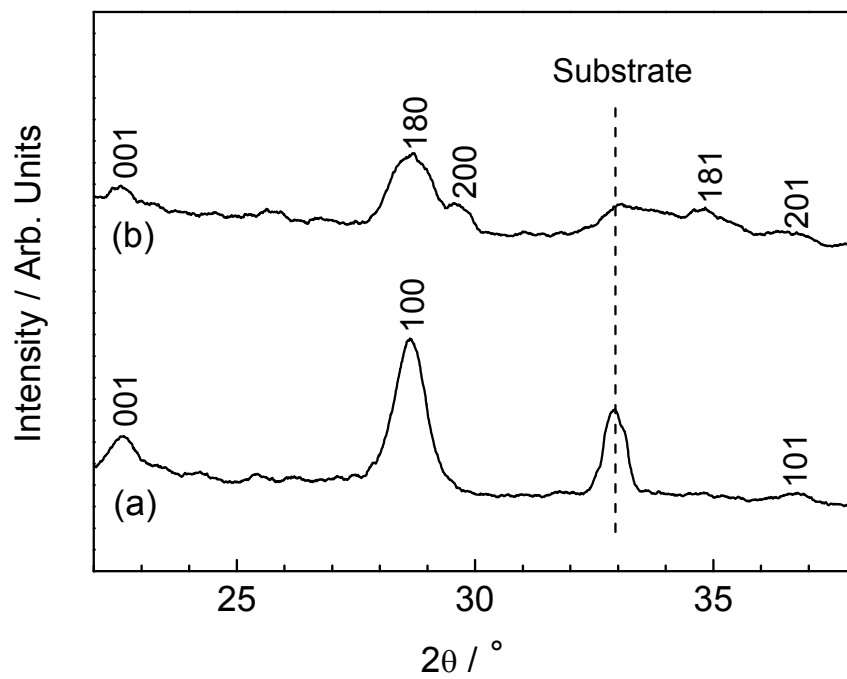


Figure S3 Wide-angle XRD patterns of mesoporous niobia thin films after calcination at (a) 500 °C (with a pseudo-hexagonal TT-Phase) and (b) 600 °C (with a orthorhombic T-phase). The peak appeared at around 33 ° is derived from the silicon substrate. Because weak (250) and (260) reflections of T-Phase exist at around $2\theta = 33^\circ$, the peak derived from the Si substrate seems to be widen.

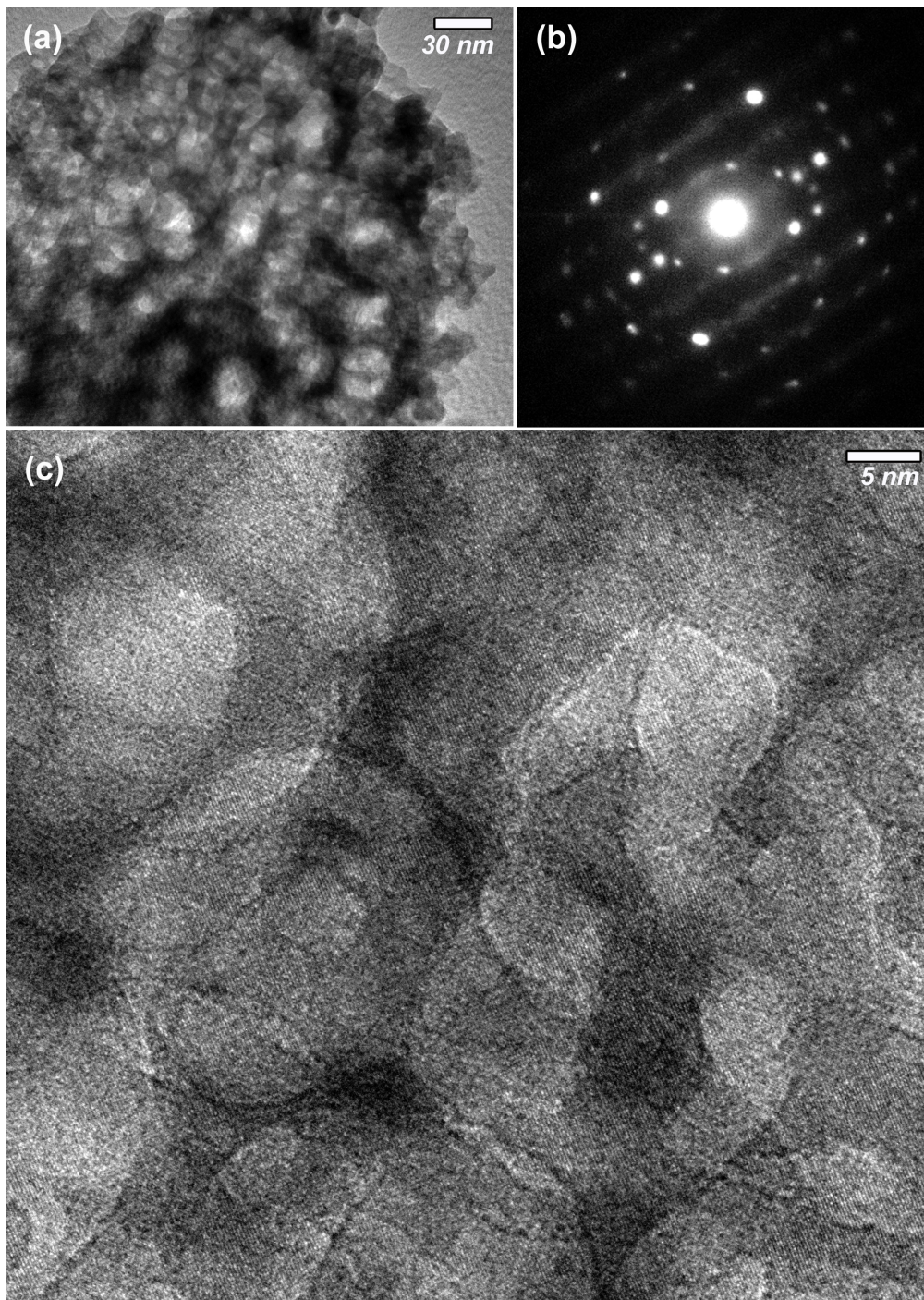


Figure S4 TEM images and the corresponding ED patterns of mesoporous niobia thin films after calcination at 500 °C (with a pseudo-hexagonal TT-Phase). The ED patterns can be assigned to be a pseudo-hexagonal TT-Phase.

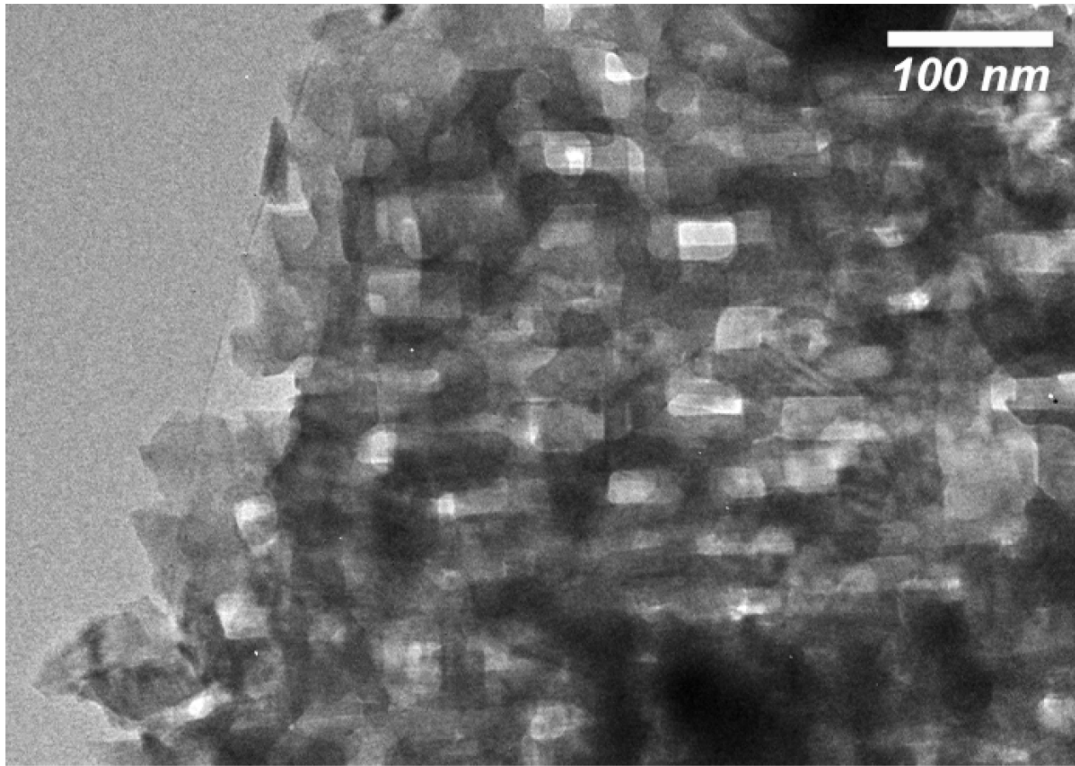


Figure S5 TEM image with the incident electron beam perpendicular to the long axis of the cuboid shaped mesopores of mesoporous niobia thin films after calcination at 600°C (with an orthorhombic T-phase). The observed area is different area from **Figures 4b**. The cuboid shaped mesopores are successfully formed over the entire area.

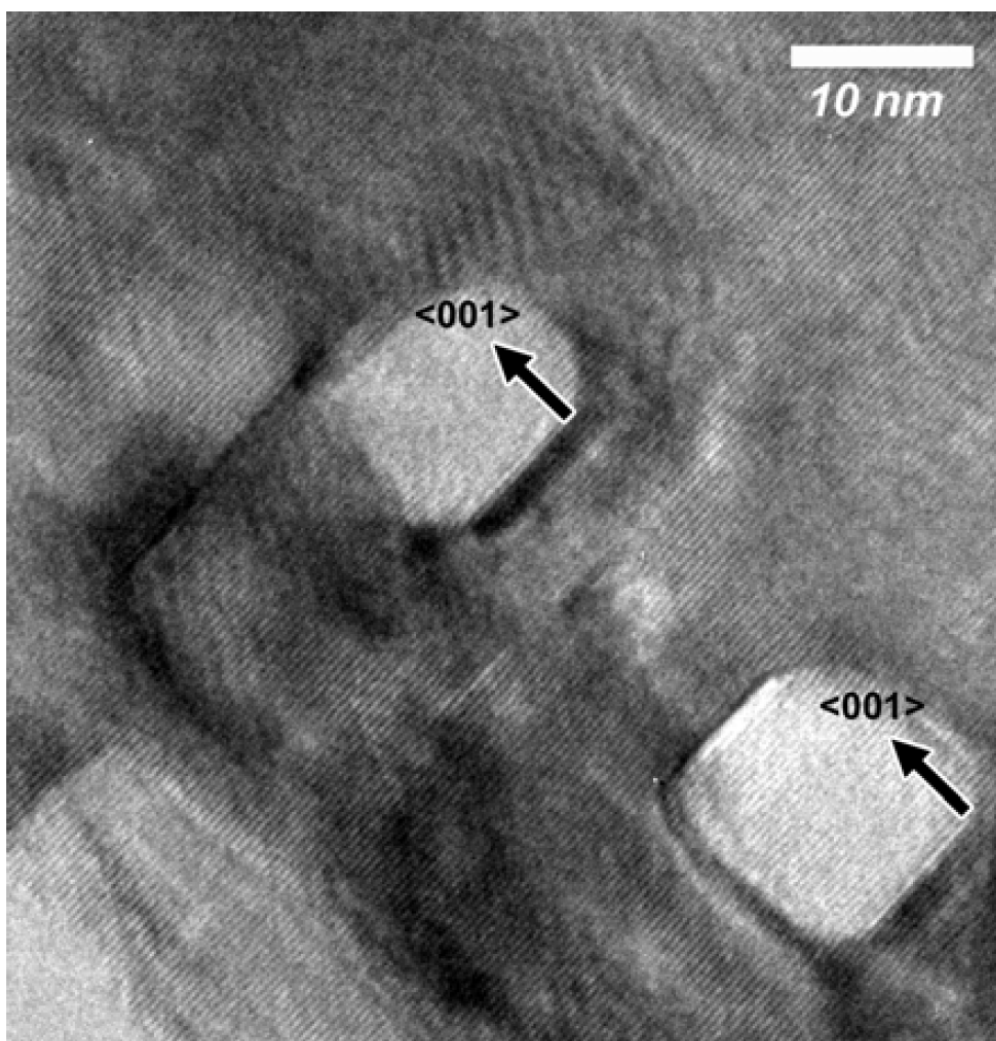


Figure S6 Highly magnified TEM image with the incident electron beam parallel to the long axis of the cuboid shaped mesopores of mesoporous niobia thin films after calcination at 600°C (with an orthorhombic T-phase). The <001> facet planes are exposed on both the mesopores. The observed area is different area from **Figure 4**. Since the mesopore is tilted to the incident beam, the lattice fringes are observed inside the mesopore range.