

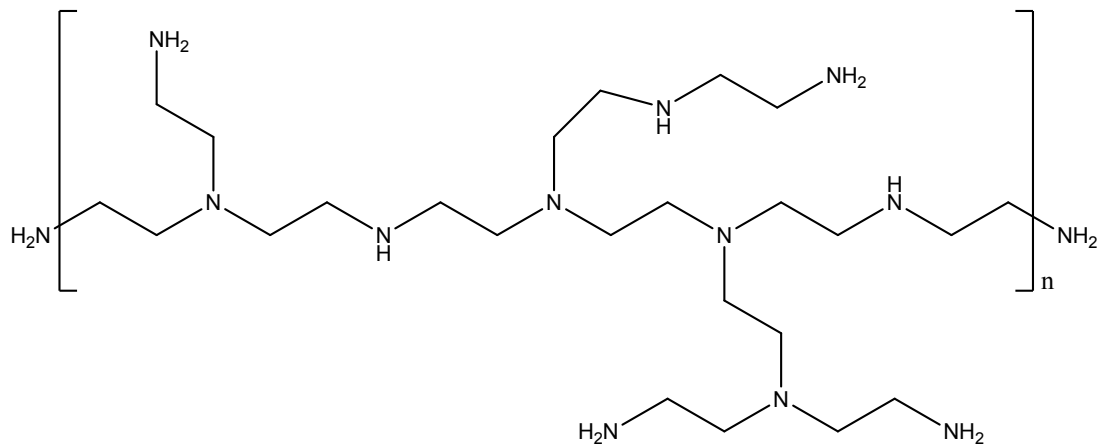
Supplementary materials

Experimental Section

In a typical synthesis, the solution of 0.5 g of P123 and 5 g of water was stirred for 4 hours at room temperature. Then, 15 g of 2M HCl was added and stirred at 40 °C for 2 hours. Subsequently, 1.5 g TEOS was added and stirred at 40 °C for 15 min. After that, a monolayer colloidal crystal template with different sphere diameters (200 nm, 500 nm and 1000 nm) heated at 100 °C for 10 min was immersed for about 3 min. The final template was picked up and dried at 100 °C for 24 hours. For the CN material, 30 wt% linear type polyethylenimine (C_2H_5N)_n - molecular weight ca. 2000, Scheme 1) in distilled water was employed as CN precursor. This precursor solution was dropped onto the surface of the above macro-mesoporous template obtained and then, the templates with precursor solution were polymerized at 100 °C about 6 h and 160 °C about 6 h, respectively. Subsequently, the resulting solids were carbonized at 450 °C for 5h with the heating rate of 3 °C/min in argon atmosphere. After dissolution of the silica framework in 10 wt% hydrofluoric acid about 2 hours, the CN film can be obtained. However, the nitrogen content of the final product is a bit lower than the original composition of the PEI because of the low thermodynamic stability of nitrogen in the carbon framework at a high temperature. When the carbonization temperature reaches to 450 °C in argon atmosphere, the PEI/PS is decomposed into NH₃, H₂O, CO₂, and C_{3.5}N. The liberated gases were removed by flowing argon gas during the carbonization process. The hydrogen content of the sample calculated from the CHN analysis is ca. 3wt.% which reduced to 2.1 wt% when the temperature is increased to 600 °C. The morphology of the films prepared at different synthesis conditions was observed on a Hitachi S-4800 field emission scanning electron microscope (FESEM). The TEM micrographs were obtained on a JEL-2100F field emission high-resolution transmission electron microscope (TEM) equipment with a Gatan-766 electron energy-loss spectrometer (EELS). The X-ray diffraction (XRD) pattern was collected on a Rigaku diffractometer using Cu K α ($\lambda=0.154$ nm) radiation. FT-IR spectrum was recorded on a Nicolet Nexus 670 instrument. X-ray photoelectron spectroscopic (XPS) analysis was performed on Perkin-Elmer PHI-5600ci.

The adsorption properties of porous CN material prepared at 450 °C toward various volatile substances were investigated using a quartz crystal microbalance (QCM) (USI System, Japan). The QCM resonators coated by silver on both surfaces were taken as electrodes and the change of one frequency corresponds to that of about 0.95 ng in mass. For our experiment, the CN film with 0.3 μ g was detached from the substrate in water and transferred to the QCM resonators. Then, it was inserted in the QCM instrument resonator holder. At the same time, desired volatile liquids (10 ml) in a glass bottle were put in the through of the QCM instrument. To prevent vapor leakage, the QCM instrument was fully covered during the *in situ* adsorption measurement. After the gas adsorption process, both the cover and the glass bottle

containing the testing solution was removed that exposed the film to the normal air. All experiments were carried out in an air conditioned room at 25 °C. Ozonization of the CN material was carried out using an ozone cleaner (Filgen UV253S system, Japan). The oxygen, UV lamp and nitrogen were introduced in order with about 15 minutes, 20 minutes and 5 minutes, respectively.



Scheme 1: Molecular structure of polyethylenimine

Figure S1

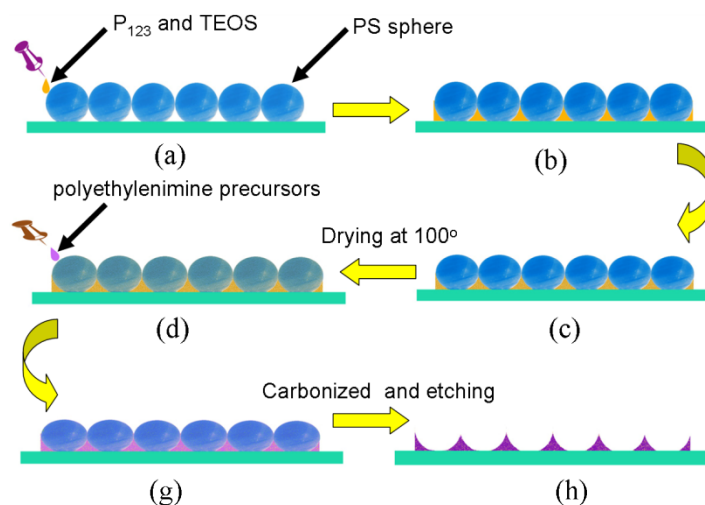


Figure S1. Schematic illustration of the synthesis of macro-mesoporous carbon nitride film. Briefly, to obtain macro-mesoporous solid template, the solution containing the silica source (TEOS) and P123 was added to the monolayer colloidal crystal template. The hybrid macro-mesophase template was formed from the inorganic phase (TEOS), the structure-directing agent (P123) and the physical template of polystyrene sphere. Following immersing the CN precursor in the hybrid macro-mesophase template, the resulting template was polymerized and carbonized at a high temperature. Finally, the macro-mesoporous CN was obtained after dissolving the mesoporous silica framework in aqueous HF. Obviously, the morphology, structure and the thickness of the CN film can be easily tuned by the simple adjustment of the size of the PS template and the controlling the PS template with different layer number.

Figure S2

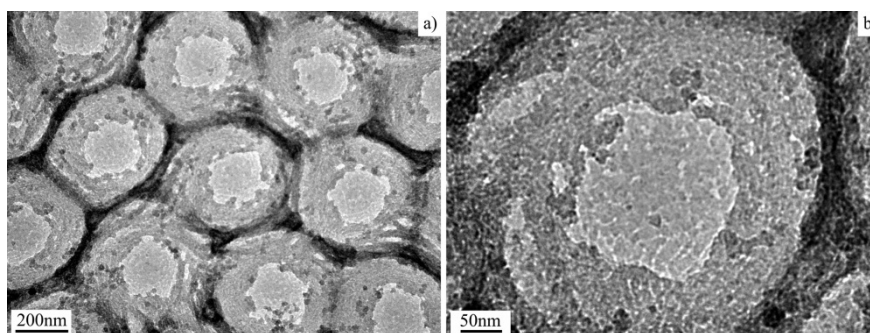


Figure S2. TEM Images of macro-mesoporous CN film: (a) low-magnification, (b) high-magnification.

Figure S3

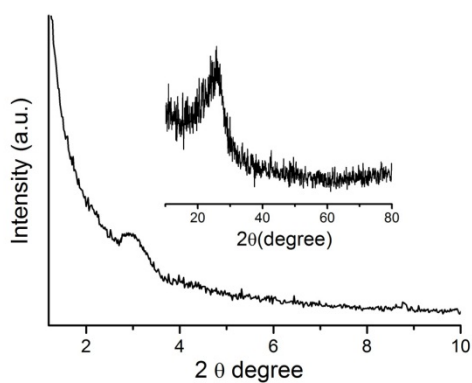


Figure S3. XRD patterns of macro-mesoporous carbon nitride film obtained at 450 °C (Inset: High angle XRD pattern).

Figure S4

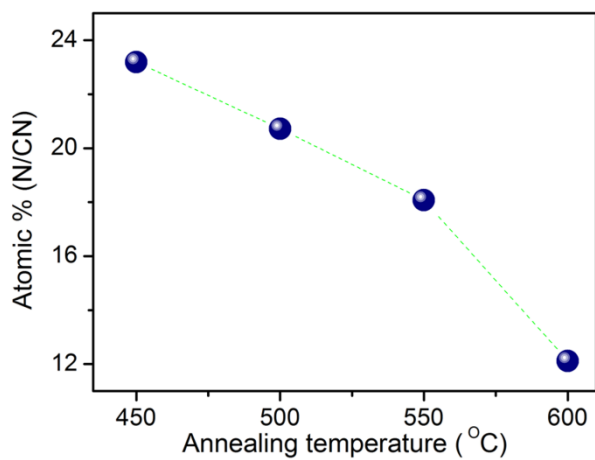


Figure S4. The curve of N/C atomic ratio vs carbonization temperature.

Figure S5

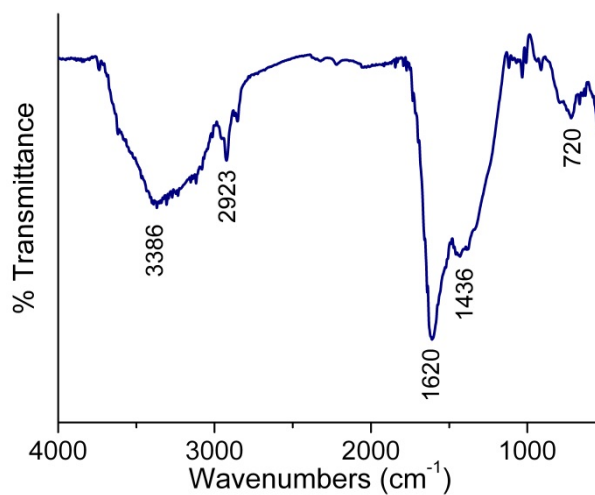


Figure S5. FT-IR spectra of macro-mesoporous carbon nitride film.

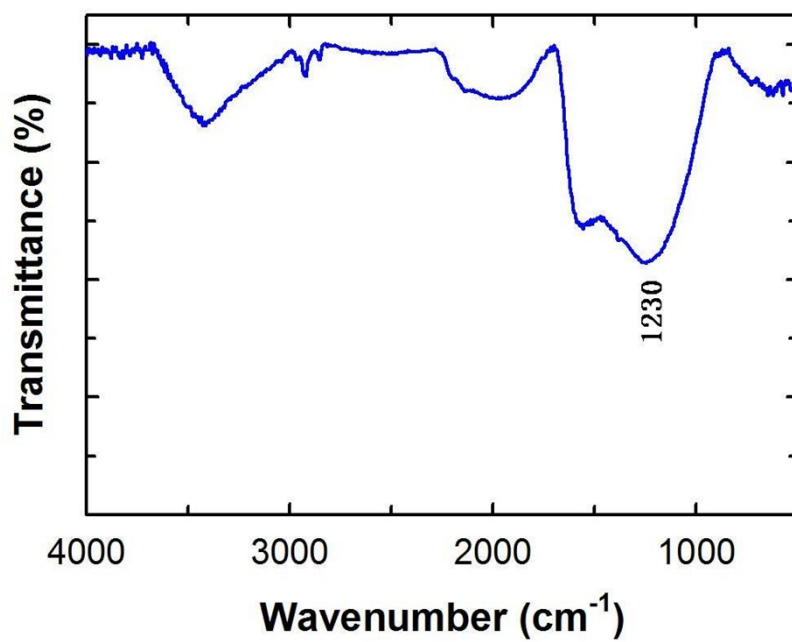


Figure S6. FT-IR spectra of oxidized macro-mesoporous carbon nitride film.

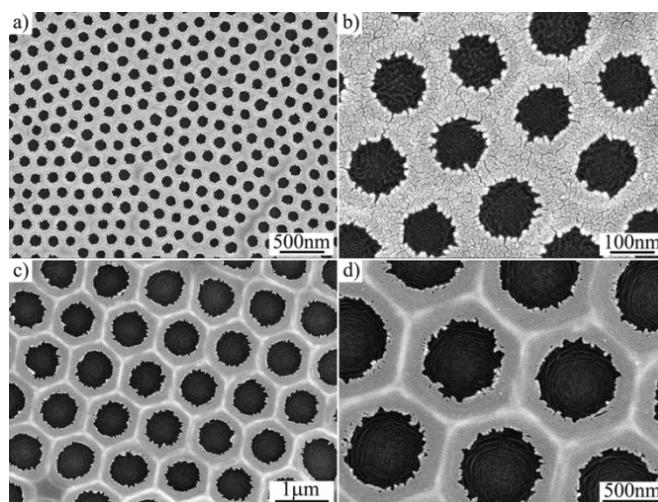


Figure S6. FESEM images of macro-mesoporous CN films with different macropore size: (a, b) 200 nm, and (c, d)1000 nm.