**Experimental**

**Alucone MLD:** Trimethylaluminum (TMA) and ethylene glycol (EG) were used as reactants for aluminum alkoxide (alucone) molecular layer deposition (MLD) at 100 °C. A fluidized bed reactor was used to deposit alucone films on SiO$_2$ particles. For a typical run, ~10 g of 250 nm SiO$_2$ particles (Sigma Aldrich) were loaded into the reactor. The particles were fluidized at a superficial gas velocity of 0.8 cm/s. During the MLD reaction, TMA (97 %, Sigma Aldrich) was fed through the gas distributor of the reactor based on the driving force of its room-temperature vapor pressure. Due to the low room-temperature vapor pressure of EG (anhydrous, 99.8%, Sigma Aldrich), a bubbler was applied to dilute the heated EG vapor stream and allowed for vapor delivery to the reactor in a controllable fashion, preventing the overdose of the precursor. A flow rate of 4 sccm of N$_2$ was sufficient to deliver EG, which was pre-heated to 80 °C, to the reactor. A typical coating cycle used the following sequence: TMA dose, N$_2$ purge, evacuation; EG dose, N$_2$ purge, evacuation. 50 cycles of alucone coating were carried out. A detailed description of the experimental procedure for MLD coating of alucone films has been described elsewhere.$^1$

**Porous structure formation:** SiO$_2$ particles with 50 cycles of alucone MLD film were soaked in deionized H$_2$O at room temperature to form a porous structure by decomposition of the hybrid polymer films. In the test, for every sample, 0.5 g of particles were placed in a 30 mL vial and soaked in 5 mL deionized H$_2$O. The alucone coated SiO$_2$ particles were soaked in deionized H$_2$O at room temperature for 1, 3, 5, 7 and 9 days, respectively. After given times, particles were filtered and vacuum dried. The pH value of the filtrate was measured by one SevenEasy pH meter (Mettler Toledo, Switzerland). The aluminum concentration in the filtrate was directly measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Applied Research Laboratories ICP-AES 3410+, and several drops of nitric acid were added to the filtrate to insure that the aluminum was not precipitating out of the samples.

Porous structure was also formed by the oxidation of the hybrid films in air. The thermolysis of alucone MLD films was carried out using a Theta Gravitronic II Thermal gravimetric analyzer (TGA). The powder sample was loaded into an alumina crucible suspended from a microbalance by a Pt wire and heated at the rate of 1°C min$^{-1}$ in a tube furnace from 25°C to a target temperature. An air stream was allowed to flow downward across the crucible at 200 sccm to promote the oxidation of the hybrid polymer films.
Characterization: Cross-sectional TEM samples were prepared by cutting epoxy resin cured particles using a diamond knife. The samples were visualized with a JEOL 2010F 200 kV Schottky field emission transmission electron microscope equipped with an Oxford detector unit for elemental analysis while imaging. The porous structure of the alucone coated SiO$_2$ particles after treating was characterized by -196 °C nitrogen adsorption and desorption isotherms for surface area and pore size distribution analysis using a Quantachrome Autosorb-1. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distributions of micropores and mesopores were calculated by the Horvath-Kawazoe (HK) model and the Barrett-Joyner-Halenda (BJH) model, respectively.

Estimated Surface Area (SA) of Porous Film Itself

Silica particles before MLD coating, SA=25.9 m$^2$/g
Porous films formed by oxidation in air at 400 °C, SA=191.6 m$^2$/g
Concentration of porous films on particles, ~13.2 wt.%

Porous film itself, SA= (191.6-25.9)/13.2% = ~1250 m$^2$/g

Reference

Fig. S1 Energy dispersive spectroscopy (EDS) spectra of (a) uncoated silica particles, (b) 50 cycles of alucone MLD coated silica particles, and (c) 50 cycles of alucone MLD coated silica particles after being soaked in water for 1 day.
Fig. S2 (a, b) Scanning transmission electron microscopy (STEM) images of 50 cycles of alucone MLD coated 250 nm SiO$_2$ particles after being soaked in water for 1 day.
Fig. S3 Surface area of 50 cycles of alucone MLD coated 250 nm SiO$_2$ particles after being soaked in water for different times.

Fig. S4 Nitrogen adsorption and desorption isotherms of 50 cycles of alucone MLD coated 250 nm SiO$_2$ particles after being soaked in water for different times.
Fig. S5 The permeance of the tubular alumina support coated with porous films.

Fig. S6 Thermal gravimetric analysis (TGA) of 50 cycles of alucone MLD coated 250 nm SiO₂ particles at 400 °C.
Fig. S7 Energy dispersive spectroscopy (EDS) spectra of 50 cycles of alucone MLD coated 250 nm SiO₂ particles after oxidation in air at (a) 400 °C and (b) 1000 °C.
Fig. S8 Transmission electron microscopy (TEM) images of 50 cycles of alucone MLD coated SiO$_2$ particles (a) before and (b, c, d) after oxidation in air at 400 °C.

Fig. S9 Nitrogen adsorption and desorption isotherms of 50 cycles of alucone MLD coated 250 nm SiO$_2$ particles after oxidation in air at 400 and 1000 °C.