

## Supporting Information

### Topological transformation of thioether-bridged organosilicas into functional nanoporous materials\*\*

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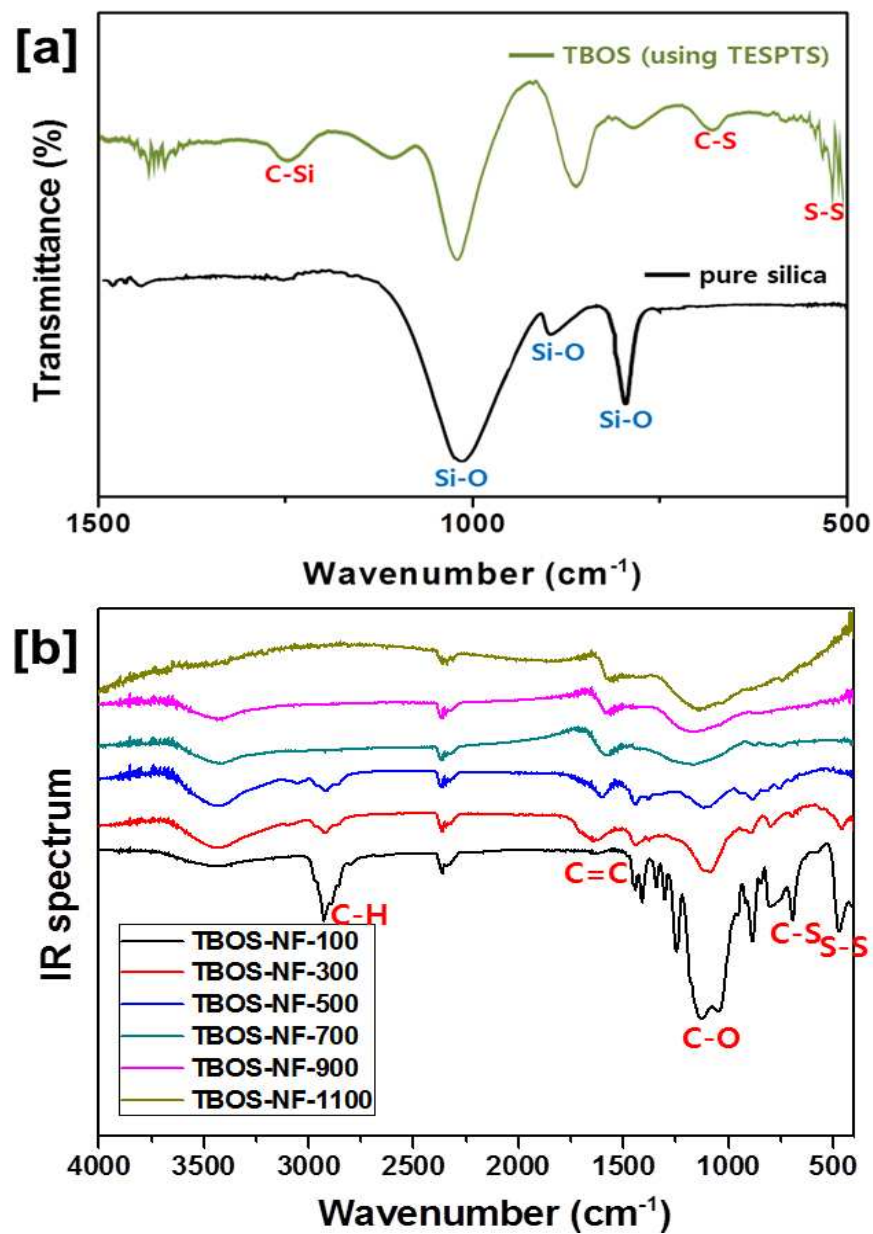
## 1. Experimental: surface characterization and electrochemical tests

Transmission electron microscopy (TEM) images were obtained by an EM912 Omega electron microscope with an acceleration voltage of 120 kV. The powder of samples for TEM measurements was ground in a mortar, suspended in ethanol and then loaded onto copper grids with carbon type B films. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4700 microscope operated at an acceleration voltage of 10 kV and HR-SEM images by using ultra high resolution-scanning electron microscope (Hitachi S-5500) operated at 30 kV. Nitrogen adsorption-desorption isotherms were measured at 67 K using a KICT SPA-3000S system. Specific surface areas of the samples were determined by nitrogen adsorption branch in the relative pressure range from 0.05 to 0.2 using the Brunauer-Emmett-Teller (BET) equation. Total pore volumes were determined from the amount of gas adsorbed at the relative pressure of 0.99. Pore size distribution (PSD) was calculated from adsorption branch by the Barrett-Joyner-Halenda (BJH) method. Powder X-ray diffraction (XRD) patterns of the samples were recorded by using a Rigaku 1200 diffractometer with Cu K $\alpha$  radiation using a Ni  $\beta$ -filter at a scan rate of 0.2 °/min. The X-ray source was operated at 40 kV and 20 mA. Fourier transform infrared (FT-IR) spectra in transmission mode were measured on a NICOLET FT-IR spectrometer by using pressed KBr tablets. Each of the IR spectra was the average of 32 scans at a speed of 2 s per scan. The resolution of the spectrometer was set to 4 cm<sup>-1</sup>. The <sup>29</sup>Si and <sup>13</sup>C cross polarization (CP) magic-angle spinning (MAS) NMR spectra were obtained on a Bruker DSX-400 spectrometer at room temperature with a 4 mm zirconia rotor spinning at 6 kHz (resonance frequencies for <sup>29</sup>Si and <sup>13</sup>C CP MAS NMR spectra were 79.5 and 100.6 MHz, respectively), 90° pulse width of 5  $\mu$ s, contact time of 2 ms, and a recycle delay of 3 s for both the <sup>29</sup>Si and <sup>13</sup>C CP MAS NMR spectra.

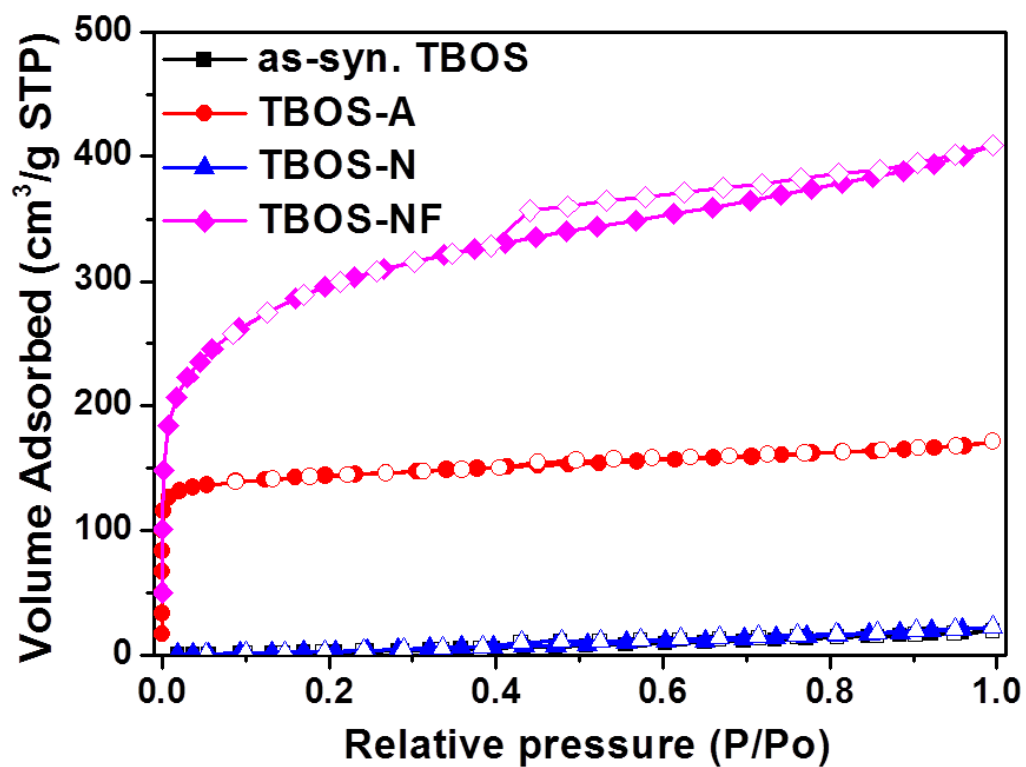
A three-electrode electrochemical cell was employed for estimation of the electrochemical surface area (ECSA), catalytic activity towards oxygen reduction reaction (ORR), and electrochemical stability of various carbon-supported Pt (60 wt%) catalysts using the rotating disk electrode (RDE)

technique. The working electrode was a thin layer of Nafion-impregnated catalyst cast on a glassy carbon disk (3 mm in diameter) embedded in a Teflon cylinder, in which Pt gauze was used as a counter electrode and Ag/AgCl as a reference one. The catalyst layer was prepared as follows: 5 mg of carbon-supported Pt catalyst was dispersed in 1 mL of a mixture solution of deionized water and ethanol (1:4 in volume ratio) and then mixed with 50  $\mu\text{L}$  of Nafion solution (5 wt% Nafion). After being ultrasonicated for 1 h, 5  $\mu\text{L}$  of the catalyst slurry was pipetted and spread on the top of a glassy carbon disk. Finally, the catalyst-loaded glassy carbon electrode was dried at 80  $^{\circ}\text{C}$  for 1 h to yield a loading of 63  $\mu\text{g Pt}/\text{cm}^2$ . Cyclic voltammetric (CV) measurements were conducted in  $\text{O}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  at room temperature with a scan rate of 50 mV/s for the determination of catalytic activity towards ORR. During the electrochemical measurements which were conducted at room temperature, the freshly prepared working electrode was immersed in the electrolyte, and then the electrolyte solution was de-aerated by purging with nitrogen for 30 min. CV was then conducted with potential sweeping between -0.2 and 1.2 V at 50 mV/s in the presence of constant  $\text{N}_2$  bubbling, and the electrode surface was determined to be clean when a reproducible voltammogram was recorded. Following the CVs in  $\text{N}_2$ , the  $\text{H}_2\text{SO}_4$  solution was saturated with oxygen through constant bubbling for 30 min before a set of CVs were recorded in the presence of  $\text{O}_2$  using the same scanning rate and same potential range as with  $\text{N}_2$  for comparison. For ORR activity measurements, linear sweep voltammetry (LSV) were conducted between -0.2 and 1.2 V at 5 mV/s in  $\text{O}_2$ -saturated  $\text{H}_2\text{SO}_4$  solution at various rotating speeds.

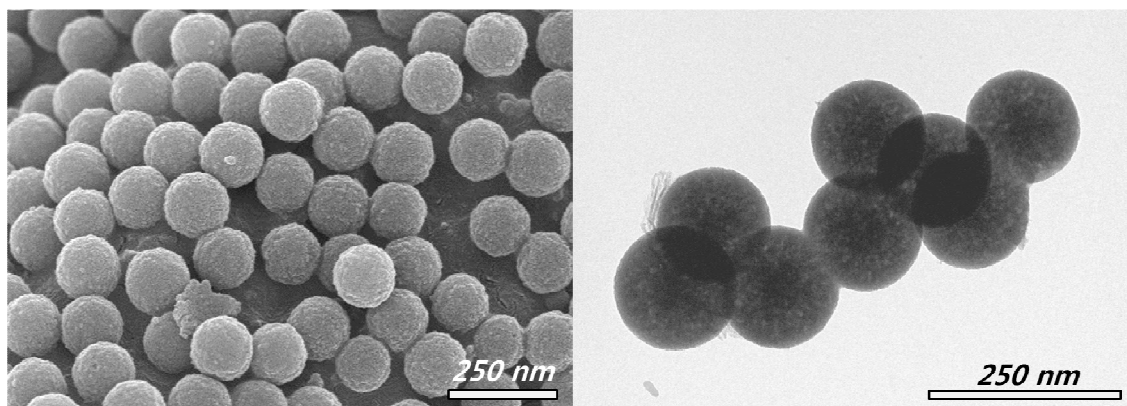
## 2. Results



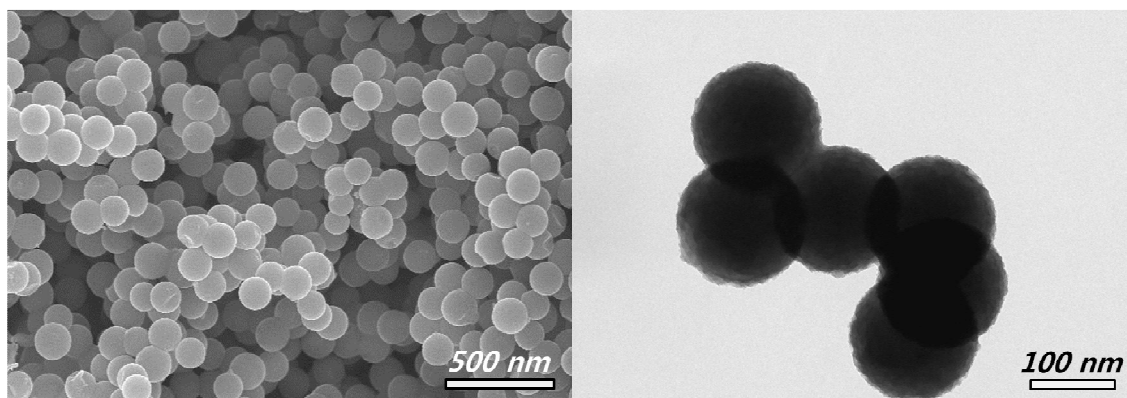
**Figure S1.** FT-IR spectra for as-synthesized TBOS and pure silica spheres (a), and TBOS samples calcined in  $\text{N}_2$  at different temperatures followed by etching silica (b).



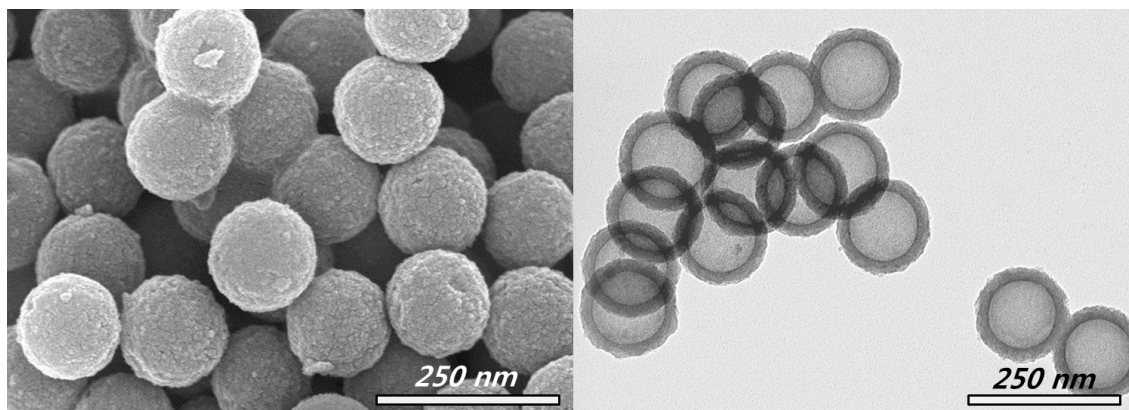
**Figure S2.** Nitrogen adsorption-desorption isotherms for as-synthesized and calcined TBOS under different (air or N<sub>2</sub>) atmospheres, and N<sub>2</sub>-calcined silica-free TBOS after silica etching treatment.



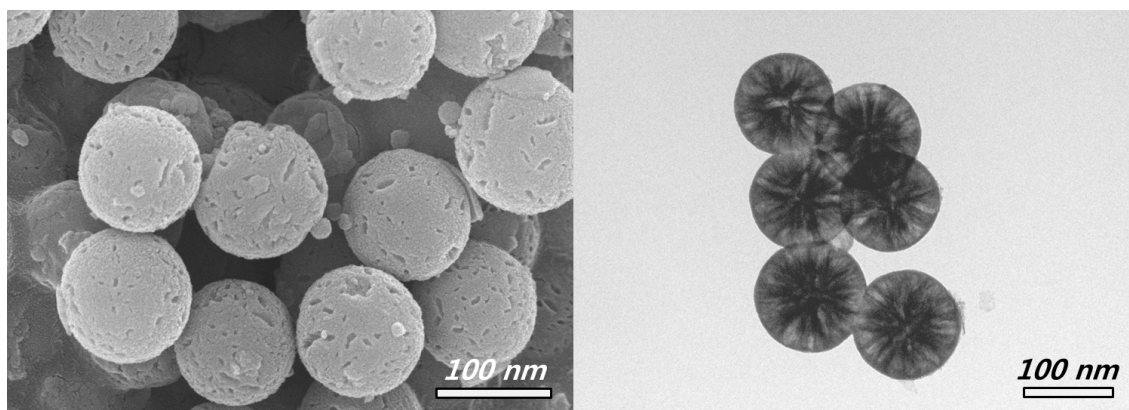
**Figure S3.** SEM and TEM images for as-synthesized CTAB-TESPTS organosilica.



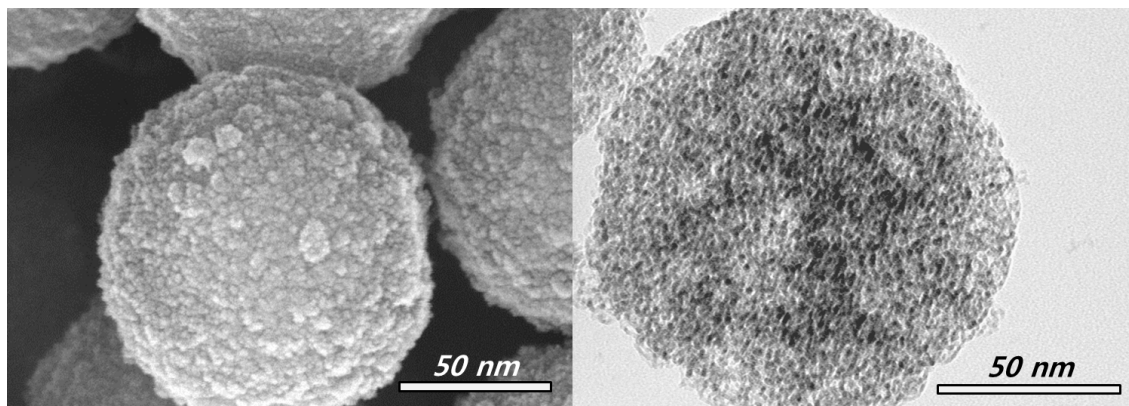
**Figure S4.** SEM and TEM images for as-synthesized C<sub>18</sub>TMS-TESPTS organosilica.



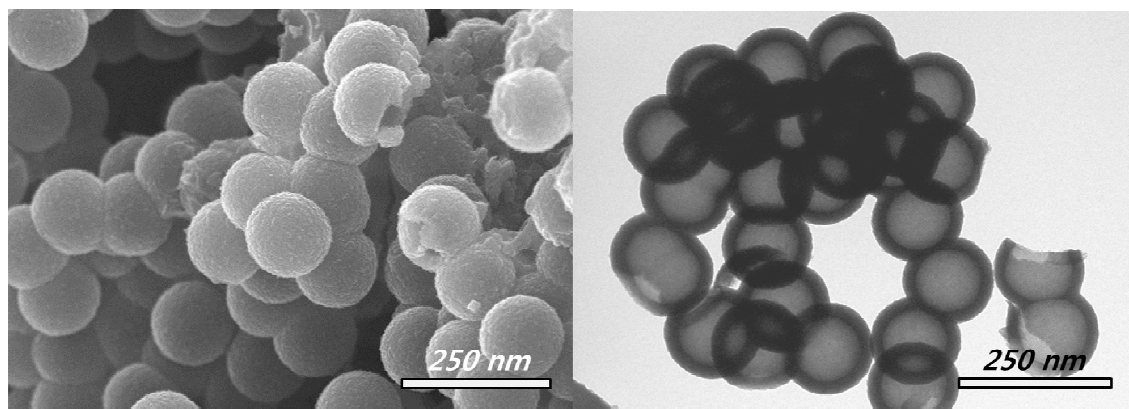
**Figure S5.** SEM and TEM images of air-calcined CTAB-TESPTS-A silica.



**Figure S6.** SEM and TEM images of  $N_2$ -calcined CTAB-TESPTS-NF carbon.

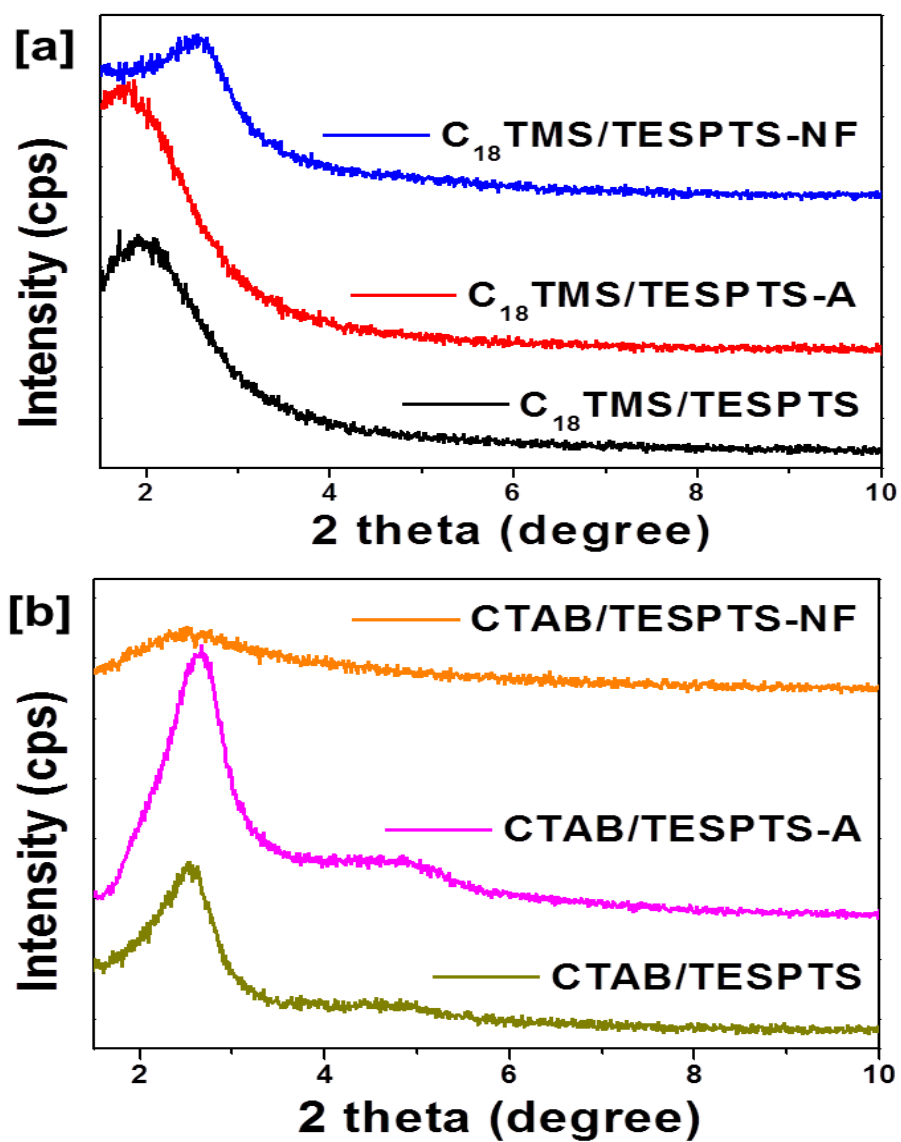


**Figure S7.** SEM and TEM images for air-calcined C<sub>18</sub>TMS-TESPTS-A silica.

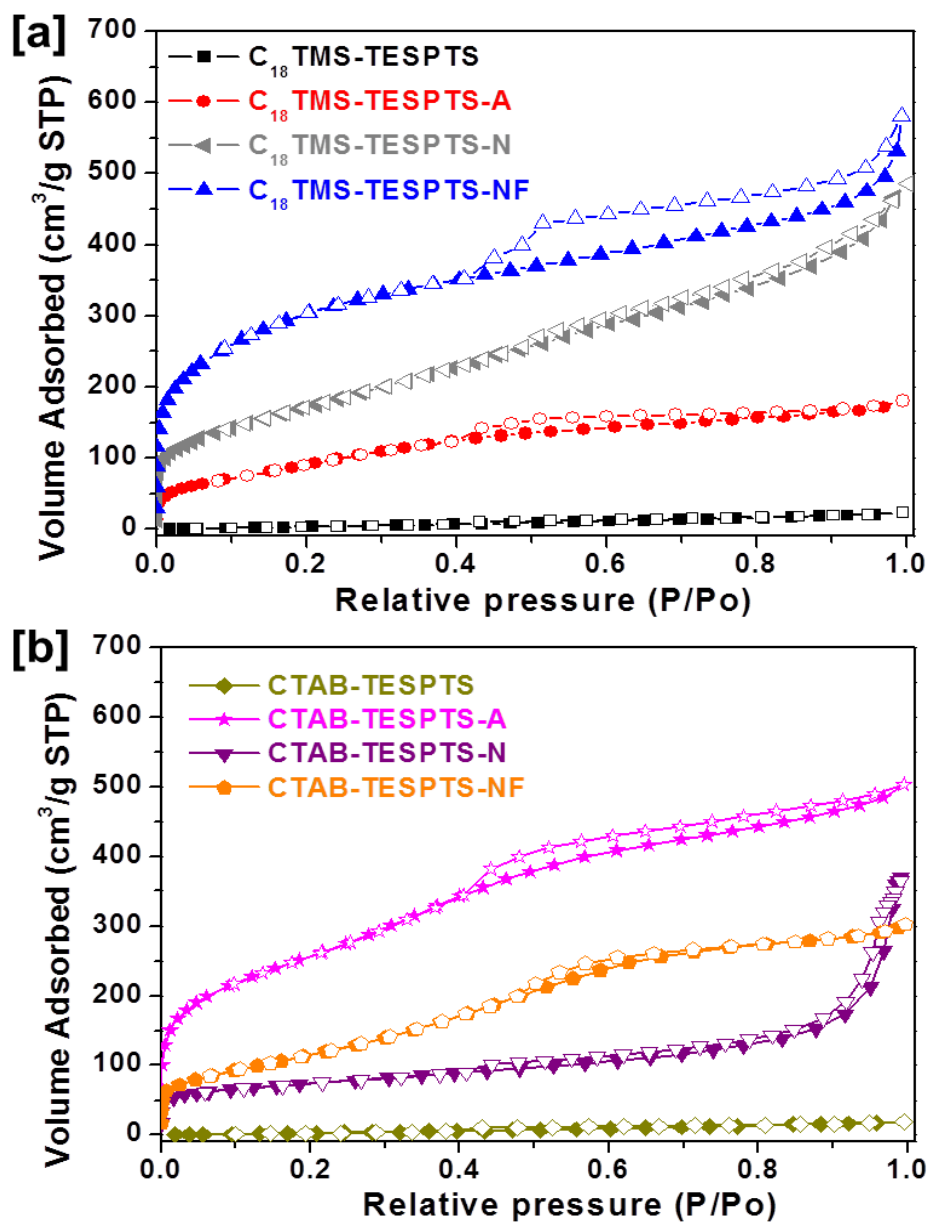


**Figure S8.** SEM and TEM images of N<sub>2</sub>-calcined C<sub>18</sub>TMS-TESPTS-NF carbon.

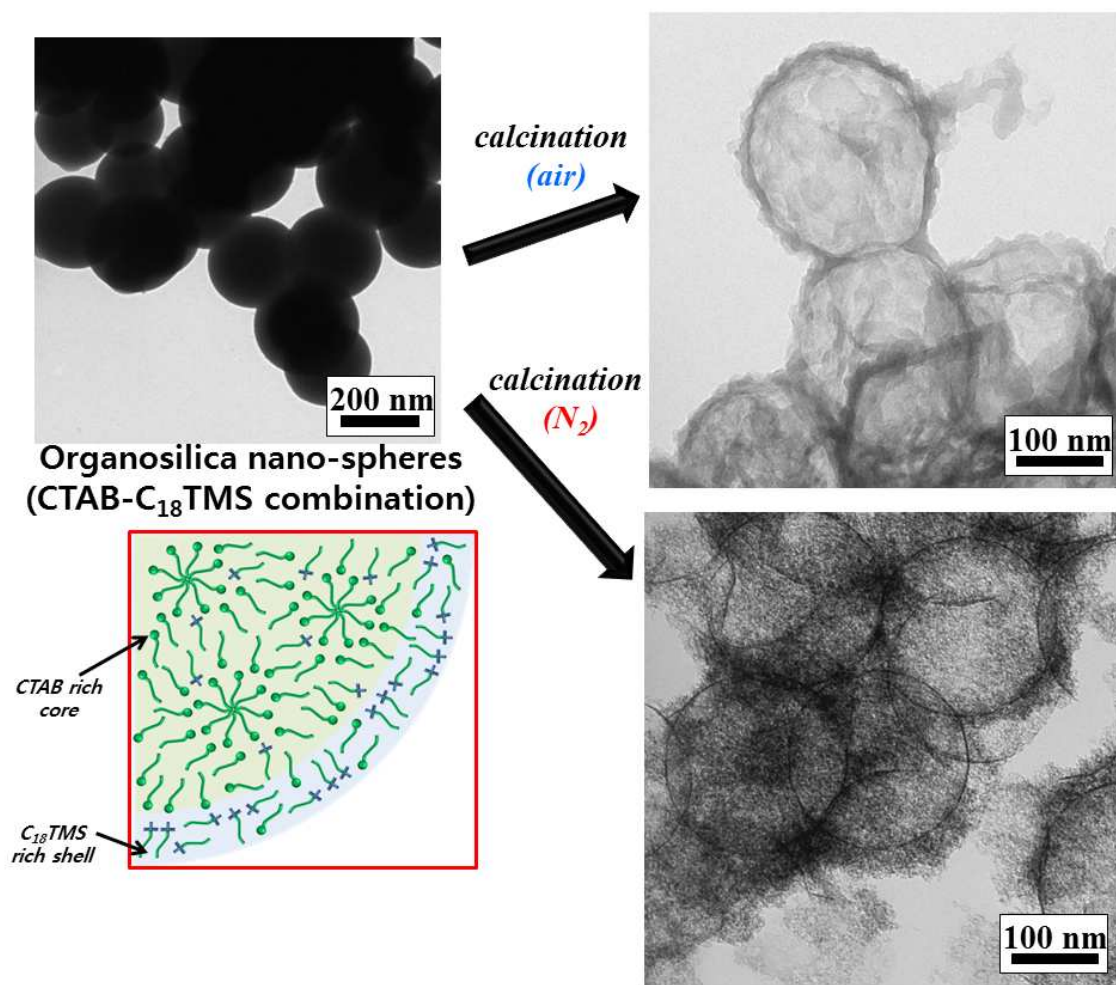




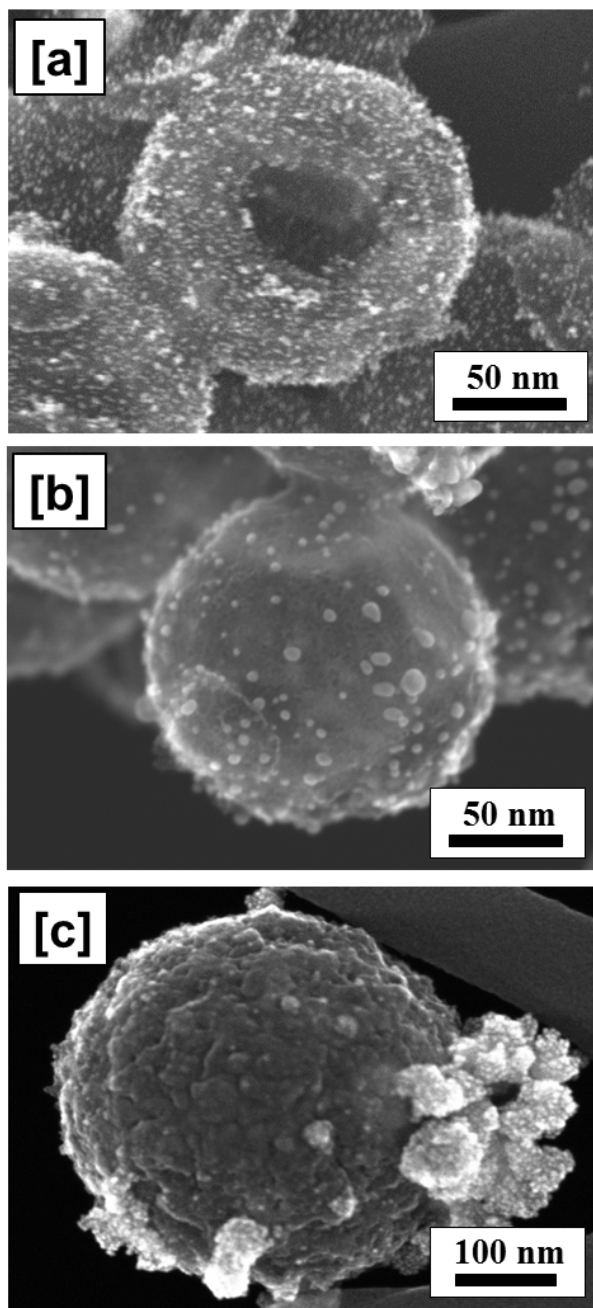
**Figure S9.** XRD patterns for as-synthesized and calcined  $C_{18}$ TMS-TESPTS (a) and CTAB-TESPTS (b) based nanostructured materials after different treatments.



**Figure S10.** N<sub>2</sub> adsorption-desorption isotherms for the as-synthesized and calcined C<sub>18</sub>TMS-TESPTS (a) and CTAB-TESPTS (b) based nanostructured materials after different treatments.



**Figure S11.** Typical TEM images of as-synthesized CTAB-C<sub>18</sub>TMS organosilica and air/N<sub>2</sub>-calcined nanostructured materials.



**Figure S12.** Representative HR-SEM images for Pt (60 wt%) deposited on the various catalyst supports, (a) C<sub>18</sub>TMS-TESPTS-NF carbon, (b) CTAB-TESPTS-NF carbon, and (c) TBOS-NF carbon.