Supporting Information

Interpretation on Nanoporous Network Structure in Rice Husk Silica Layer: A Graph Model

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The rice used in this study was harvested from suburban areas of Gwangju in Republic of Korea from 2006. The cultivar of rice was Seomyeong (Gyehwa30). The gas permeance through the raw husk silica layer has been determined experimentally using individual rice husk samples epoxied to a 2 mm diameter end of a glass tubing attached to a vacuum system equipped with capacitance manometers and a mass spectrometer. From the observed permeation of gases before and after a treatment of the husk sample with hydrogen fluoride solution, the permeance of the silica layer for hydrogen is estimated. The silica layer which was used in measurements of BET, ^{29}Si NMR, and XRD was isolated as follow. 3g of washed and dried rice husk was reacted with 0.1mol $Na_2Cr_2O_7 \cdot 2H_2O$ in cleaning solution at 298K for 1 d. Then the solid part was separated, washed, and dried. After that, it was treated twice in Aqua regia at 298K for 1 d. The silica was washed with distilled water and absolute ethanol. There was no trace of Na or Cr in XRF spectra. In comparison to this, rice husk silica from pyrolysis obtained from an acid treatment at 360K, carbonization at 620K, and oxidation in air at 1070K of the rice husk. The inner structure of the silica layer was investigated with 200 KeV or 300 KeV high resolution TEM. The rice husks were washed with acetone and cured at 25°C for 12 hrs after imbedding in epoxy resin. The microtomed sections (approximately 100–150 nm thickness) were cut from the embedded specimen by an ultramicrotome using a diamond knife at room temperature and then collected onto polyvinyl formal resin film on 200-mesh copper grids. The specimen was thinned by ion milling to prepare for high resolution TEM.

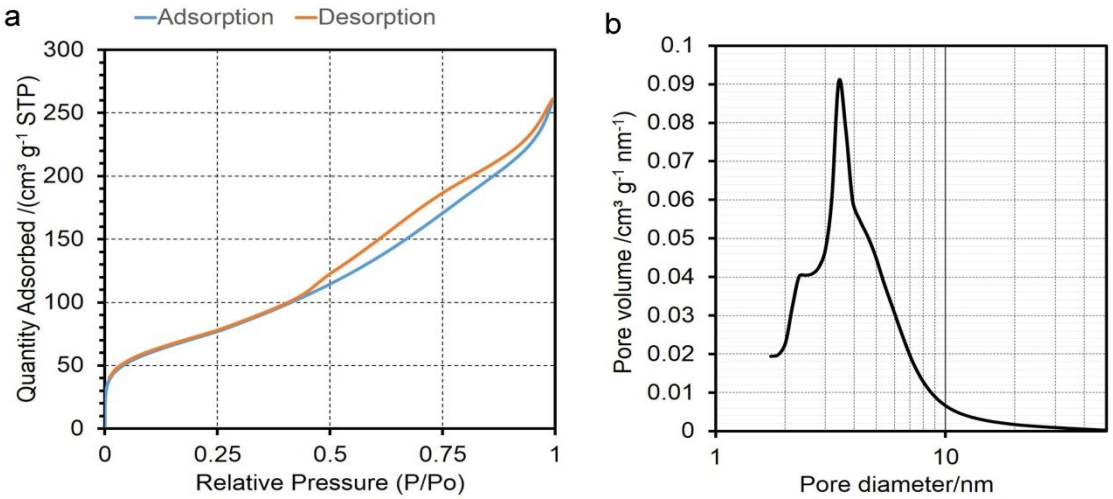

Figure S1. Adsorption and desorption of N_2 at 77K on the silica layer in rice husk.

a, Adsorption-desorption curves with BET surface area (A), single point adsorption pore volume (V) at P/P_0 = 0.9917, and adsorption averaged pore width (4V/A) as 267 m^2g^{-1}, 0.372 cm^3g^{-1}, and 5.6 nm, respectively.[8] **b**. The pore distribution of the silica layer in rice husk plotted by BJH method. The peak maximum of the pore diameter appears at ~ 3.5 nm. The silica layer was isolated from a chemical decomposition of organic layers in the rice husk.

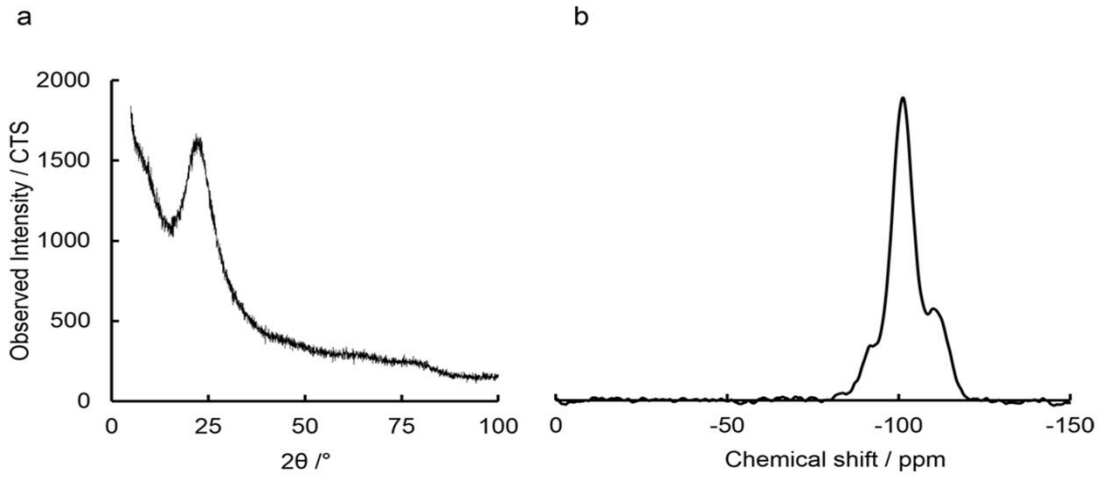

Figure S2. **Long range structure of the silica layer.**

a, X-ray diffraction pattern of the layer with a broad peak with d spacing about 0.4 nm (2θ = 22).

b, ^{29}Si NMR spectrum of the layer with three broad peaks at – 92 ppm, - 101 ppm, and -110 ppm that correspond to Q^2, Q^3, and Q^4 states of Si, respectively. The silica layer was isolated from a chemical decomposition of organic layers in the rice husk.

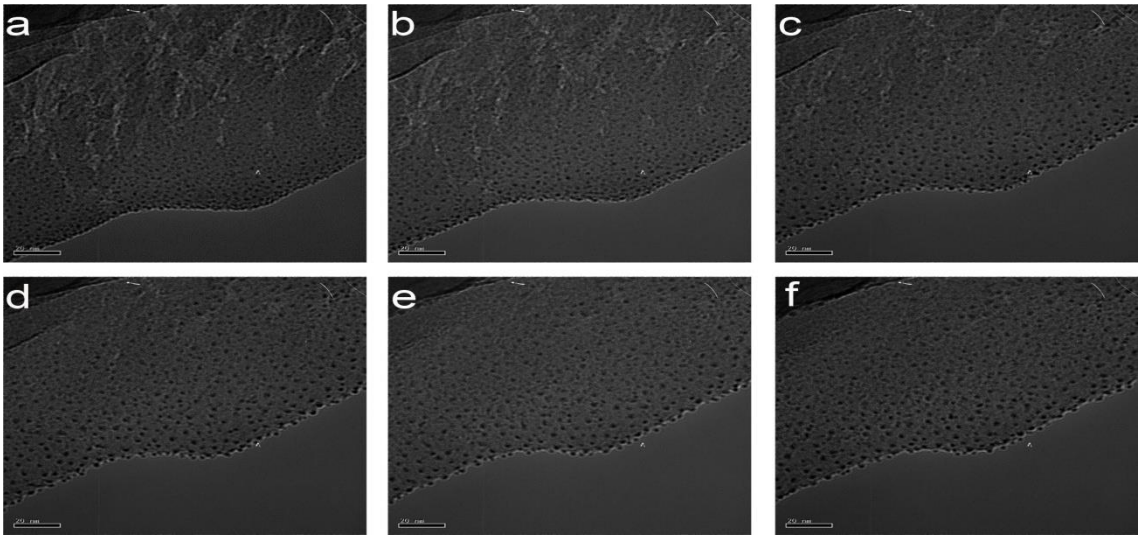

Figure S3. Change of the TEM image of an edge of the silica layer during electron irradiation. The decrease of white area can be interpreted as the collapse of the porous network. The black dots of ~ 2 nm may be corresponded to the traces of the entrances of the tunnels. The size of images, 160 nm x 160 nm. The irradiation time of electron beam becomes longer in the sequence of **a, b, c, d, e** and **f**.

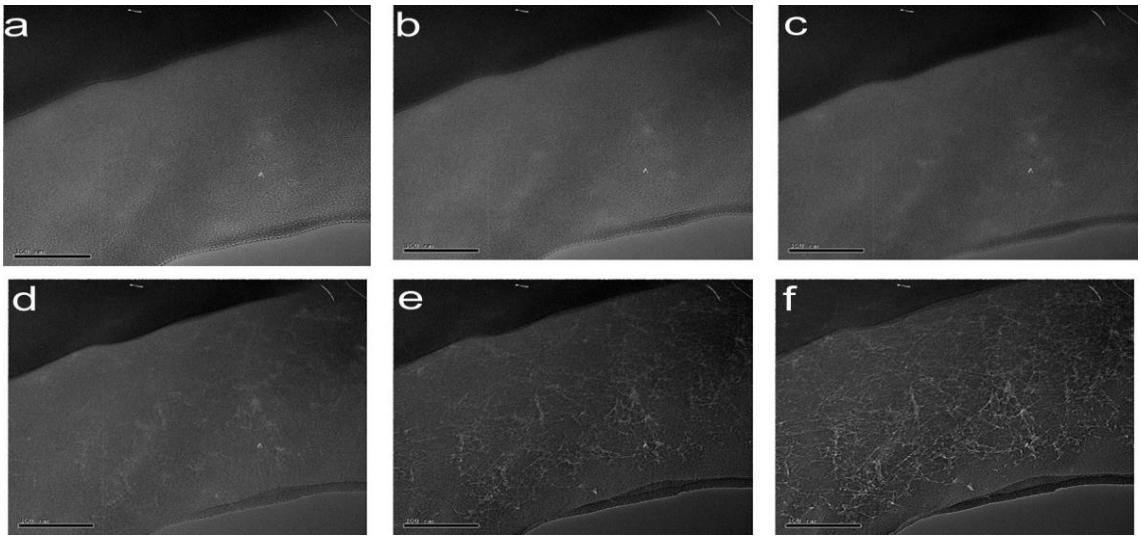

Figure S4. Change of the TEM image of the silica layer depending on the focusing depth. The appearance of the white pattern in the adjustment of the focusing depth supports the void network in the layer. The size of images, 500 nm x 500 nm. The focusing depth of electron beam becomes deeper in the sequence of **a, b, c, d, e** and **f**.

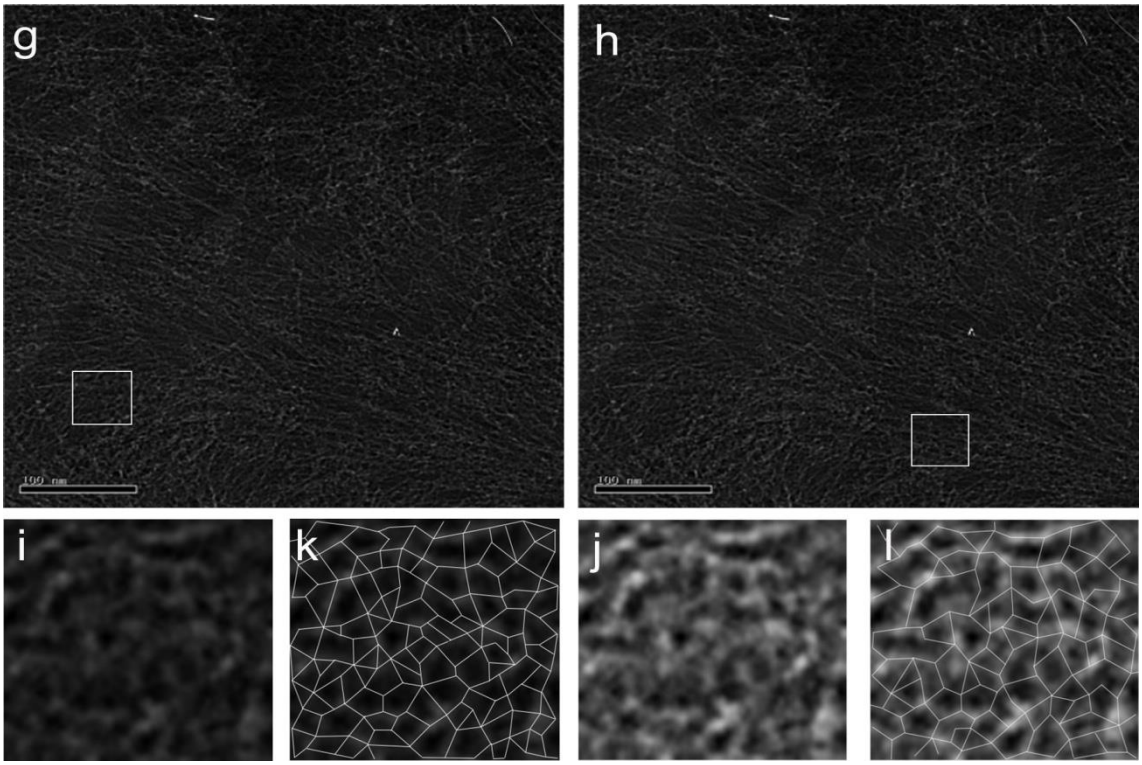

Figure S5. Examples of the development of spheres and tunnels network model for the silica layer in rice husk. g, **h**; TEM images of the cross section of the silica layer in rice husk (25,000×). **i**, **j**; Expanded image of the rectangular parts in **g**, **h**, respectively. **k**, **l**; Graphs overlapped on **i**, **j**, respectively. Scale bars in **g**, **h**; 100 nm. The size of images **i, k, j, l**; 50 nm × 50nm.