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Structural Analysis of Sulfonated Mesoporous Silica

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[Introduction]
Mesoporous silica (MPSi) is an inorganic porous material consisting of silicon and oxygen [1]. The structure of MPSi has hexagonally ordered cells as shown in Fig. 1, and the continuous and solid cell provides a fine but ample reaction space in the mesopores. The mesopore size (diameter and cylinder depth) is controllable [2]. In addition, the solid shell of MPSi prevents from the external environment (see Fig. 1). On the other hands, we have already developed a new composite polymer electrolyte membrane, synthesized from combination of sulfonated mesoporous silica (SMPSi) and hydrocarbon polymer [3]. These membranes show high protonic conductivity. We consider that H_2O molecules attached on the inner mesopore surface cause the conductive pathways of the protons. Such useful merits of the SMPSi with the proton conductive polymer membrane are recently expected to be used for a new type of a fuel cell. As we have already demonstrated, we know that the SMPSi after oxidative treatment process improves on the protonic conductivity [4]. In this paper, we report the experimental results for the SMPSi after the oxidative treatment process with transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometer (EDS). We especially aimed at identifying the location of sulfur of SO_3H groups in SMPSi.

[Experimental]
Specimens for electron microscope analysis are sliced from the SMPSi embedded in epoxy resin, to be approximately 70 nm-thick, with an Ultramicrotome UC7 (Leica Co. Ltd.). We observed fine porous structure of SMPSi by TEM and performed elemental analysis of the cross-sectional SMPSi with EDS at 200 kV. The experimental set-up we used for the experiments are field emission TEMs (JEM-2200FS, JEM-2800) and EDS (DrySD100GV, JED-2300).

[Results and Discussion]
Figure 2 shows a set of TEM images, where A1 and A2 are cross sectional views of the mesopore tubes, and A3 is a side view of the tubes. The Fourier transforms of the TEM images are displayed in the insets of corresponding images. These transforms show good three dimensional regularity of mesopore tube array. With these TEM images, mesopore diameter ϕ and interval d in SMPSi were measured to be ϕ = 7.56 nm, d = 9.57 nm. Figure 3(a) and 3(g) shows Scanning Transmission Electron Microscope (STEM) - High Angle Annular Dark Field (HAADF) images and Figs. 3(b)-(f) show the elemental maps of C, O and S analyzed by EDS for the area indicated with red rectangle in Fig. 3(a). Figure 3(g) shows the overlay of these elements. The sulfur is found to be localized at the mesopores. This clearly suggests that organic SO_3H groups located on the mesopores.
We have known that there is some correlation of the conductivity between the amount of sulfur and the acidity estimated from the ion-exchange capacity measurements. This suggests that the amount of sulfonic acid group in the mesopores directly improves on the conductivity by its acidity.

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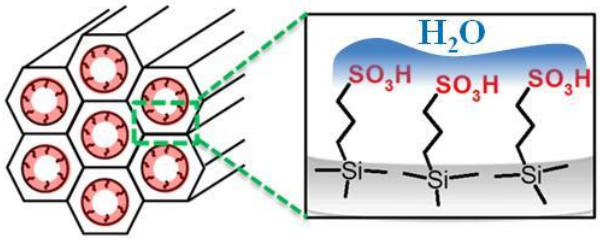

Figure 1: Structure of a sulfonated mesoporous silica (SMPSi).

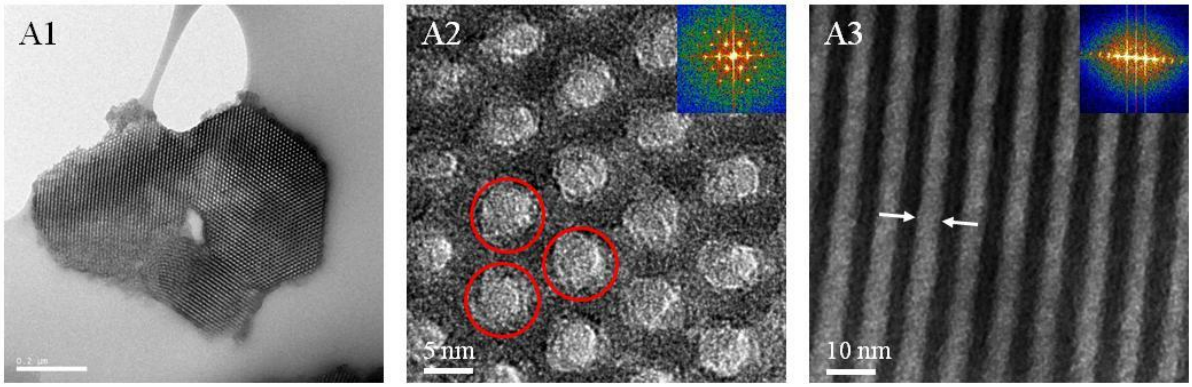

Figure 2: TEM images of SMPSi (A1 and A2: cross sectional view of the tubes, A3: side view of the tubes).

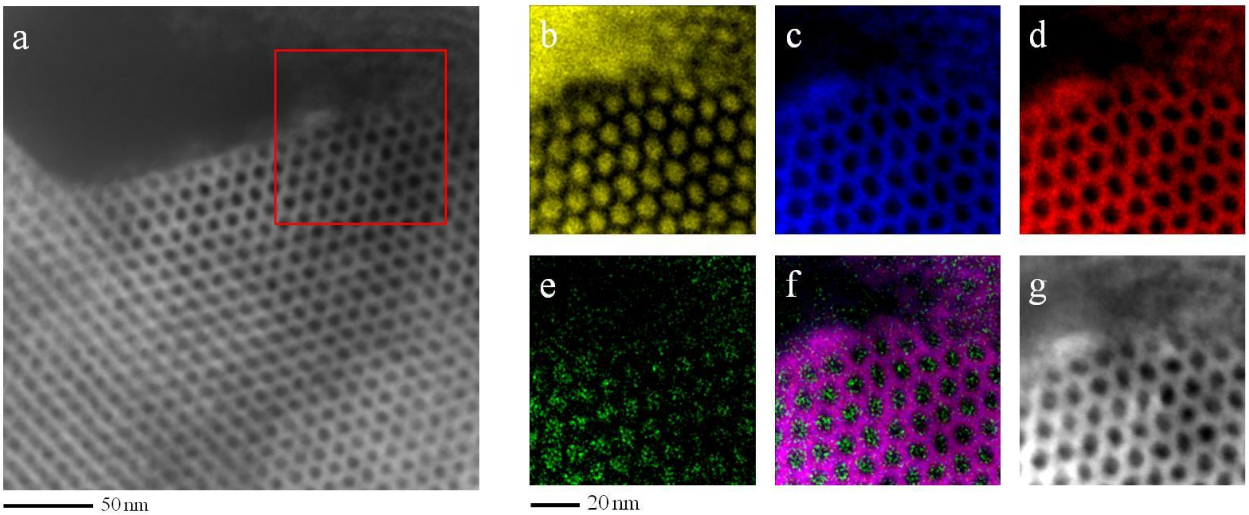

Figure 3: (a) and (g) are STEM-HAADF images and (b)-(f) are elemental maps by EDS analysis, which are from red rectangle area in (a) (b: C Kα, c: O Kα, d: Si Kα,e: S Kα, f: the overlay of c, d and e).

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