

## SUPPORTING INFORMATION

### Mechanochemical Lithiation of Layered Polysilane

Masataka Ohashi,<sup>1</sup> Hideyuki Nakano,<sup>1,2</sup> Tetsuya Morishita,<sup>3</sup> Michelle J. S. Spencer,<sup>4</sup> Yuka Ikemoto,<sup>5</sup> Chihiro Yogi,<sup>6</sup> and Toshiaki Ohta<sup>6</sup>

<sup>1</sup>Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan

<sup>2</sup>Japan Science and Technology Agency, PRESTO, Kawaguchi, Saitama 332-0012, Japan

<sup>3</sup>Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

<sup>4</sup>School of Applied Sciences, RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia

<sup>5</sup>Spring-8 Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo, Hyogo 679-5198 Japan

<sup>6</sup>SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

#### **Content of the Supporting Information:**

1. Experimental Section: chemicals, general procedures, and synthetic procedures
2. Details of the structural analysis for the obtained  $\text{Si}_6\text{H}_6/n\text{Li}$ . Figures S1–S7, color of the composites, XRD patterns of milled  $\text{Si}_6\text{H}_6$  without Li, SEM images, Infrared microspectroscopic analysis, theoretical study on the partial vibrational density of state for Si and Li in the composite and Li K-edge XANES analysis respectively.
3. References

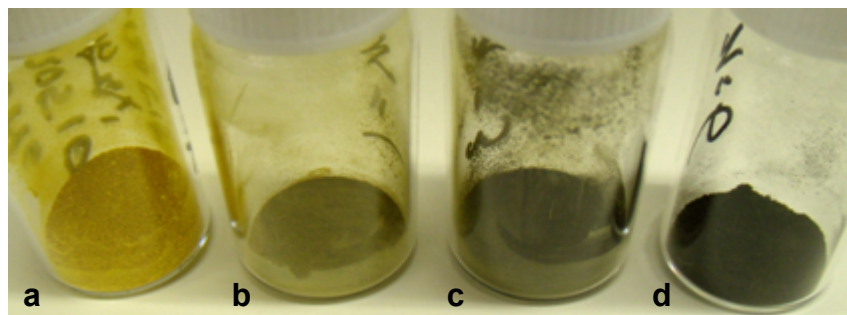
## 1. Experimental Section

**Chemicals.** All reagents and solvents were purchased from Aldrich, TCI, or Wako Chemicals and were of the highest commercial quality and used without further purification. Calcium silicide ( $\text{CaSi}_2$ ) was prepared according to the literature.<sup>1</sup>

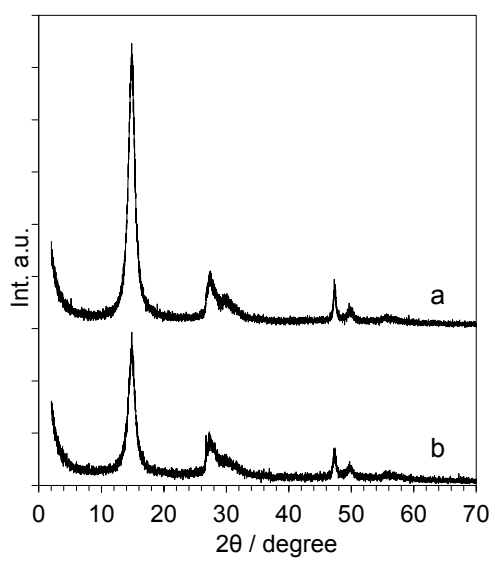
**General procedures.** Powder x-ray diffraction measurement was performed on a Rigaku RINT-TTR diffractometer with  $\text{CuK}\alpha$  radiation (50 kV, 300 mA). The UV–vis diffuse reflectance spectrum was recorded on a JASCO V-670 spectrophotometer with an integrating sphere unit (JASCO ISN-723). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS50 FT-IR spectrometer with a diamond attenuated total reflection unit. The infrared absorption spectra of the low wavenumber region were measured using a synchrotron-radiation source and the BL43IR beamline infrared microscope at SPring-8.<sup>2</sup> The infrared beam was focused on an area of approximately 20  $\mu\text{m}$  in diameter on a thin sample. The field emission scanning electron microscope (FE-SEM) image was obtained using an Hitachi S-3600N electron microscope with an acceleration voltage of 15 kV. Li K-edge and Si K-edge X-ray absorption near-edge structure (XANES) analysis was performed with the BL-2 and BL-10 double crystal monochromator beamlines at the Synchrotron Radiation Center at Ritsumeikan University. The theoretical XANES spectrum was calculated using the FEFF program. The current–voltage (I–V) profile was measured by a KEITHLEY 2636A System Source Meter. The self-supported composite disk for I–V measurement (10 mm in diameter and approximately 0.2 mm in thickness) was prepared by using a die set and miniature manual press, and the I–V curve was measured in the perpendicular direction of the disk. The diffuse reflectance UV–vis spectrum was recorded on a JASCO V-670 spectrophotometer with an integrating sphere unit (JASCO ISN-723). The samples were encapsulated in a sealed cell under argon atmosphere.

**Synthesis of layered polysilane ( $\text{Si}_6\text{H}_6$ ).**  $\text{Si}_6\text{H}_6$  was prepared according to the method described by Yamanaka et al.<sup>3</sup> Approximately 1 g of  $\text{CaSi}_2$  was immersed in 500 mL of 37% HCl. The mixture was stirred continuously at  $-30\text{ }^\circ\text{C}$  for 7 days. The obtained as-made  $\text{Si}_6\text{H}_6$  was rinsed with cooled HCl (100 ml) and dilute HF (10 ml) solution and then vacuum dried at room temperature.

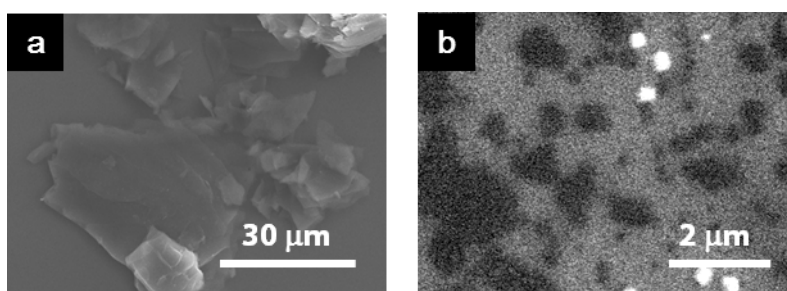
## 2. Details of the structural analysis.



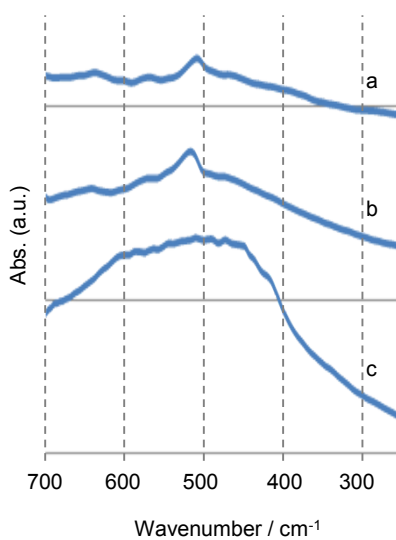
**Figure S1.** Color of the obtained composites: (a)  $\text{Si}_6\text{H}_6$ , (b)  $\text{Si}_6\text{H}_6/1\text{Li}$ , (c)  $\text{Si}_6\text{H}_6/3\text{Li}$ , and (d)  $\text{Si}_6\text{H}_6/6\text{Li}$



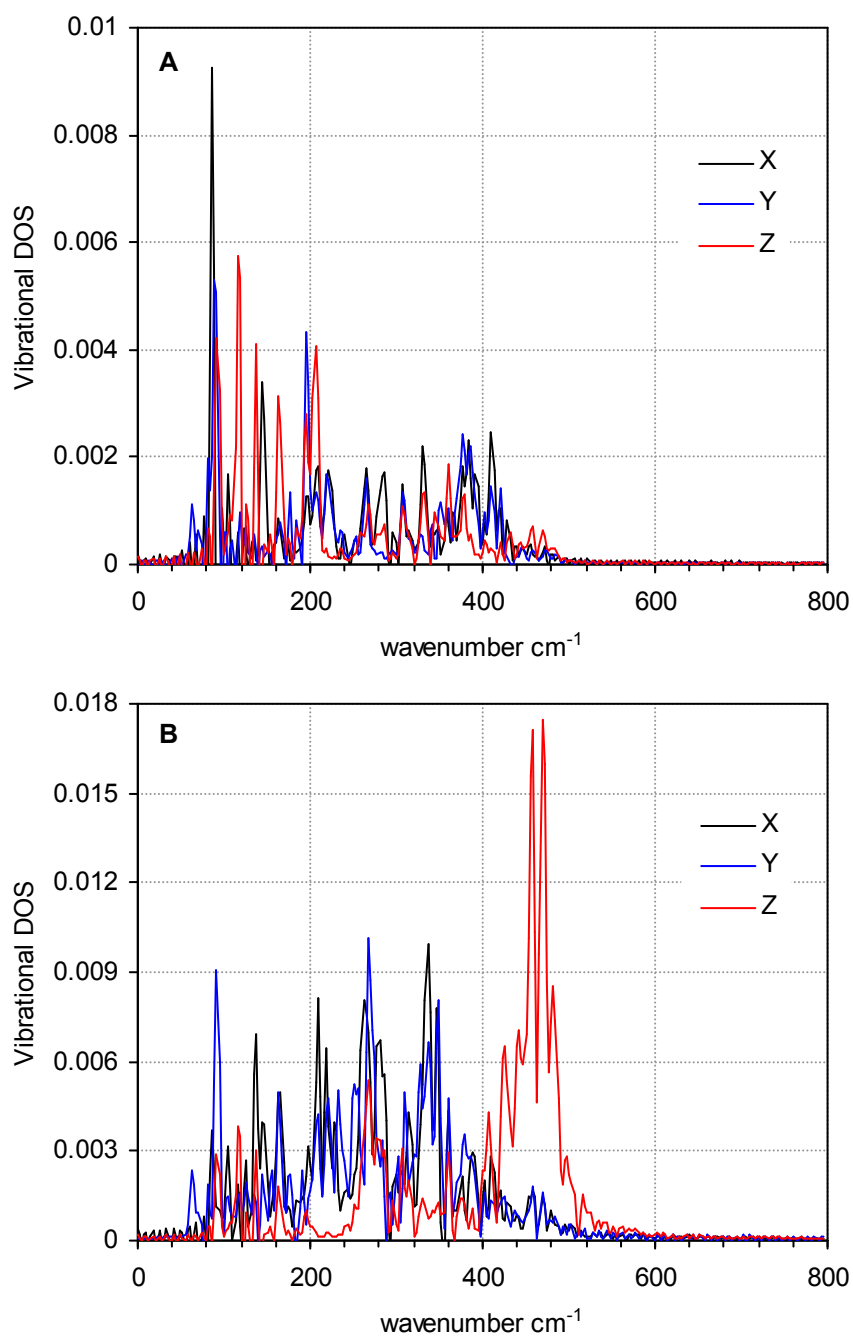
**Figure S2.** X-ray diffraction patterns of (a)  $\text{Si}_6\text{H}_6$  and (b) milled  $\text{Si}_6\text{H}_6$



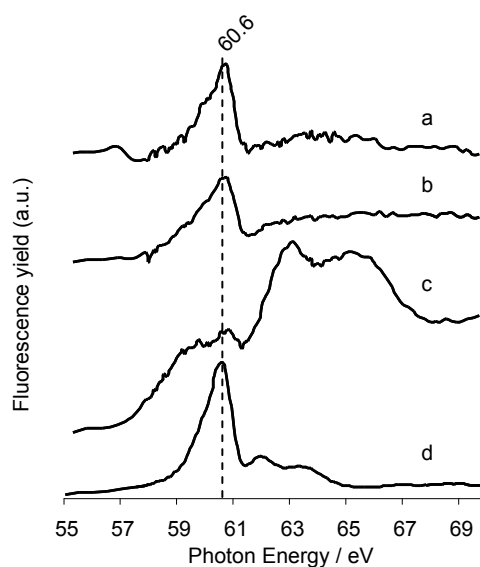
**Figure S3.** Field-emission scanning electron microscope (FE-SEM) images of  $\text{Si}_6\text{H}_6$  (a) and  $\text{Si}_6\text{H}_6/6\text{Li}$  (b). Samples for FE-SEM observation were prepared by dropping and drying  $\text{Si}_6\text{H}_6$  or  $\text{Si}_6\text{H}_6/6\text{Li}$  dispersion in THF on a flat plate. FE-SEM images of before and after the lithiation of  $\text{Si}_6\text{H}_6$  clearly suggest that the plate-like shapes of  $\text{Si}_6\text{H}_6$ , which resulted from the stacking of the layers were completely destroyed by the milling process. In addition, the aggregates of the lithiated layer were observed as atypical particles (black spots on image b).



**Figure S4.** Infrared microspectroscopic analysis of the low wavenumber region of (a)  $\text{Si}_6\text{H}_6$ , (b)  $\text{Si}_6\text{H}_6/3\text{Li}$ , and (c)  $\text{Si}_6\text{H}_6/6\text{Li}$



**Figure S5.** The partial vibrational density of state (DOS) of X, Y, and Z directions for (A) Si and (B) Li in a  $\text{Si}_6\text{Li}_6$  model calculated using *ab initio* molecular-dynamics data. The X and Y directions are parallel to the sheet surface, and the Z direction is perpendicular to the sheet surface. The calculated vibration spectra appeared at 100–500  $\text{cm}^{-1}$ . Si–Li vibration can be attributed to 450  $\text{cm}^{-1}$  due to the typical peak of the vibrational DOS of the Z direction because the Si–Li bond is present in a direction perpendicular to Si-NS.



**Figure S6.** Li K-edge XANES spectra of (a)  $\text{Si}_6\text{H}_6/\text{Li}$ , (b)  $\text{Si}_6\text{H}_6/3\text{Li}$ , (c)  $\text{Si}_6\text{H}_6/6\text{Li}$ , and (d)  $\text{LiCl}$ .  $\text{Si}_6\text{H}_6/n\text{Li}$  showed a peak attributed to the Li cation at 60.6 eV. These spectra indicated that Li exists as a cationic species in the composite. Although  $\text{Si}_6\text{H}_6/6\text{Li}$  exhibited broad peaks at 62–67 eV, we could not attribute those peaks because they changed dramatically in relation to the baseline set for the spectrum.

### 3. References.

- [1] S. Yamanaka, H. Itoh and M. Hattori, in *Expanded Clays and Other Microporous Solids*, (Eds: M. L. Occelli and H. E. Robson), van Nostrand Reinhold, New York, 1992, pp. 296–317.
- [2] H. Kimura, T. Moriwaki, S. Takahashi, H. Aoyagi, T. Matsushita, Y. Ishizawa, M. Masaki, S. Oishi, H. Ohkuma, T. Namba, M. Sakurai, S. Kimura, H. Okamura, H. Nakagawa, T. Takahashi, K. Fukui, K. Shinoda, Y. Kondoh, T. Sata, M. Okuno, M. Matsunami, R. Koyanagi, Y. Yoshimatsu and T. Ishikawa, *Nucl. Instrum. Methods Phys. Res. A*, 2001, 467–468, 441–444.
- [3] S. Yamanaka, H. Matsu-ura and M. Ishikawa, *Mater. Res. Bull.*, 1996, 31, 307–316.