Electronic Supplementary Information (ESI)

Synthesis of a calcium-bridged siloxene by a solid state reaction for optical and electrochemical properties

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Contents of the Supporting Information:

1. Experimental detail

Synthesis of Ca-siloxenes. $CaSi_2$ (3.2 mmol for CS0.25 and 0.32 mmol for CS2.5, Rare Metallic) and $TaCl_5$ (0.32 mmol, Wako Pure Chemical) were mixed together and stored in boron nitride crucibles. These mixtures were calcined at 215 °C for 5h at a heating rate of 100 °C/h which is enough to prevent temperature overshoot, within sealed stainless-steel cells (inner volume: ca. 10 cm^3). Then the products were washed with anhydrous ethanol to remove $CaCl_2$ and $TaCl_5$ or their derivatives, followed by drying under vacuum at 80 °C. All synthesis steps were carried out under Ar atmosphere.

Characterization of Ca-siloxenes. The crystalline structures of samples were characterized by XRD using a Rigaku RINT-TTR (CuKα radiation (λ=1.5418 Å), 50 kV, 300 mA). STEM and EDX analyses were performed to analyze microstructures and compositions, employing a JEOL 2010. The pore size distributions were calculated by applying the N_2 adsorption method, using a Quantachrome Autosorb-1. Raman spectra were acquired with a Jasco NRS-3300 laser Raman spectrometer and infrared spectra were obtained using a Nicolet AVATOR 360 FTIR with samples in the form of KBr pellets. Si K-edge absorption spectra were acquired at the BL6N1 line of the Aichi Synchrotron Radiation Center. During this analysis, photons from a storage ring (1.2 GeV) were monochromatized using InSb(111) crystals, samples were loaded on In foil under Ar atmosphere and the spectra were collected in fluorescence yield mode under He atmosphere. Bond distances were obtained by a fitting of the Fourier transformed k^2-weighted EXAFS spectra over a *k* range of 2.0 to 8.0 $Å^{-1}$ using the software Artemis.

Optical and electrochemical properties. UV/Vis absorption spectra were acquired with a Shimadzu S-3600N spectrometer in the diffuse reflectance mode at room temperature under air. Optical bandgap energy values were calculated based on tauc plots of the associated absorption data. The electrical conductivity values of samples were determined using the two-probe method with pelletized specimens at room temperature under air. PL spectra were obtained at room temperature under air with excitation at 442 nm and 20 mW (1 kW cm^{-2}) using a Kimmon Koha IK Series He-Cd laser and a Princeton Instrument PIXIS 400 Si-CCD detector with a cut off filter (< 495 nm) in front of the monochrometer. The Li ion capacities of samples were evaluated with a Hokuto Denko HJ1010 galvanostat at 25 °C using electrodes (sample/acetylene black = 70/30 wt%) pressed onto a Ni form. Li foil was used as the counter electrode and a 1 M solution of $LiPF_6$ in an ethylene carbonate/diethyl carbonate mixture (50/50 v/v) was employed as the electrolyte. A constant current of 0.1 A g^{-1} was applied with a voltage window of 0.02–1.50 V vs. Li/Li^+.

2. Overview of 2D Si backbone structures in siloxenes (Figure S1)

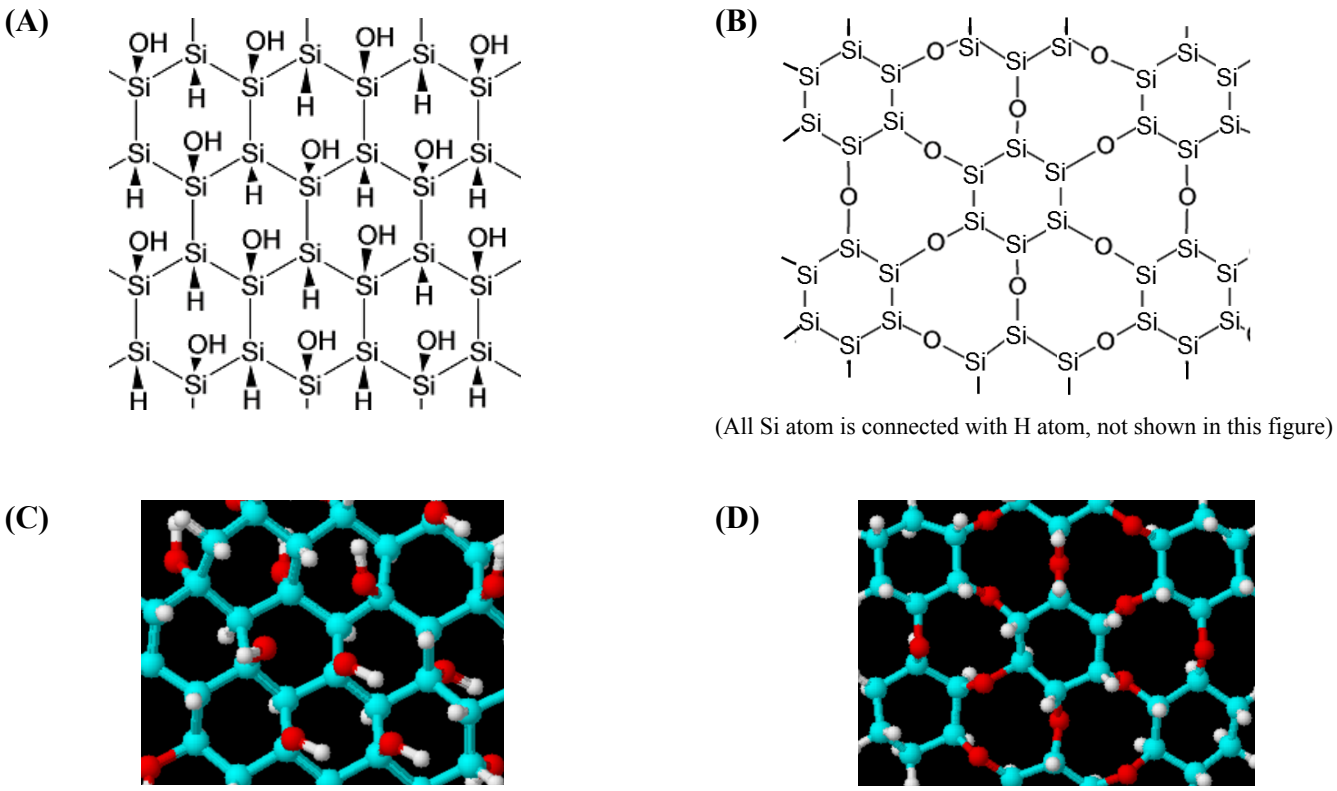

Figure S1. Si backbone structures of (A) Weiss-type and (B) Kautsky-type siloxene, and estimated partial 3D views of (C) Weiss-type and (D) Kautsky-type siloxene.

3. **N_2 adsorption desorption isotherm (Figure S2)**

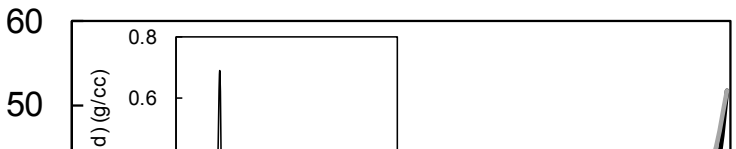

Figure S2. N_2 adsorption-desorption isotherm of CS2.5. Inset: pore size distribution.

4. **Bond distance obtained by fitting EXAFS data (Table S1)**

The k^2-weighted $\chi(k)$ function was extracted from EXAFS spectra and Fourier transformed over a k range of 2.0-8.0 $Å^{-1}$ using the software Athena. Bond lengths were obtained from fitting the Fourier transforms over a R range of 1.0-3.8 Å under the fixed condition of $\sigma_2 = 0.003$ using the software Artemis.

Table S1. Bond distance obtained by fitting EXAFS data.

	Bond length(Å)			R factor (%)
	R_{Si-O}	R_{Si-Si}	R_{Si-Ca}	
CS0.25	1.576	2.418	3.110	4.65
CS2.5	1.591	2.400	3.128	3.42
$CaSi_2$	-	2.399	3.090	5.94