Electronic Supplementary Information

Two dimensional siloxene nanosheets: Novel high performance supercapacitor electrode materials

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1. Experimental section

1.1 Materials and methods

Calcium silicide (CaSi$_2$) and tetraethylammonium tetrafluoroborate (TEABF$_4$) were purchased from Alfa Aesar Chemicals, South Korea. Hydrochloric acid (HCl) and acetonitrile (AN) were obtained from Dae-Jung Chemicals Ltd, South Korea. Ultrasound irradiation was carried out in a VCX 750 ultrasonicator (Sonics and Materials, Inc, USA, (20 kHz, 750 W)) using a direct-immersion titanium horn.

1.2 Preparation of siloxene sheets

The 2D siloxene sheets were prepared via topochemical transformation of CaSi$_2$ in ice-cold HCl [1-3]. Briefly, well-ground CaSi$_2$ powder (1 g) was immersed in conc. HCl solution (100 mL, assay 37%) under vigorous stirring at 0 °C for 4 days. A slow color transformation of the reaction mixture from black CaSi$_2$ to yellowish green confirmed the slow dissolution of Ca in HCl. After completion of the reaction, green siloxene sheets were separated via repeated centrifugation (rpm of 10,000) with acetone and water. The resulting powder was dispersed in water (100 mL) and subjected to ultrasound irradiation for 1 h. The green siloxene sheets were separated via centrifugation and then dried at 80 °C for 12 h.

1.3 Instrumentation

A Rigaku X-ray diffractometer with Cu Kα radiation operated at 40 KeV and 40 mA was used to examine the phase purity and crystallinity of the siloxene sheets. The surface morphology and elemental mapping of the siloxene sheets was investigated by FE-SEM (JSM-6700F, JEOL Instruments) and HRTEM (JEM-2011, JEOL) with a CCD 4k × 4k camera (Ultra Scan 400SP, Gatan) The surface topography and section (line profile) analysis of the siloxene
sheets were probed by AFM (Digital Instruments, Nanoscope V multimode 8) in tapping mode. The functional groups of the siloxene sheets were examined using FT-IR spectroscopy carried out on a Thermo Scientific FT-IR spectrometer (Nicolet 6700). The siloxene sheets were mixed with KBr and compressed into a transparent tablet for measurement. Pure KBr was used as the background. The chemical state of elements present in the siloxene sheets was investigated by XPS using a photoelectron spectrometer (ESCA-2000, VG Microtech Ltd.). A high-flux X-ray source of 1486.6 eV (aluminum anode) and 14 kV was used for X-ray generation, and a quartz crystal monochromator was used to focus and scan the X-ray beam on the sample surface. Raman spectra and maps were obtained using a LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France). The Raman system used an argon-ion laser operating at a power of 10 mW with an excitation wavelength of 514 nm; the data-point acquisition time was 10 s. The Raman mapping (intensity ratio maps and peak position maps) of siloxene sheets was analyzed using LabSpec (Ver. 6.2) software. The N$_2$ adsorption–desorption isotherms of CaSi$_2$ and the siloxene sheets were measured at 77 K using a NOVA 2000 system (Quantachrome, USA) and pore size distributions were calculated using the Horvath–Kawazoe method.

1.4 Electrochemical characterization

A working electrode was first prepared by grinding siloxene powder, carbon black, and polyvinylidene fluoride (PVDF) with a ratio of 90:5:5 with an appropriate amount of N-Methyl-2-pyrroldione (NMP) in an agate mortar until a uniform slurry was obtained. The slurry was spin coated on a stainless-steel current collector at 200 rpm and then dried at 80 °C for 12 h. The electroactive mass of the siloxene sheets on the stainless-steel current collector was determined from the difference between the mass of the current collector before and after siloxene loading using a dual-range semimicrobalance (AUW-220D, Shimadzu) with an approximation to five
decimal places. The mass loading of siloxene sheets was about 0.5 mg in each electrode. The thickness of the siloxene on the current collector was about 7 µm, as measured using a NanoView high-accuracy 3D nano non-contact surface profiler. The siloxene SSC device was fabricated with a CR2032 coin cell configuration using siloxene-coated stainless-steel substrates with area of 1.86 cm² as electrodes separated by a Celgard membrane and 0.5 M TEABF₄ in acetonitrile as the electrolyte. The fabricated SSC device was crimped using an electric coin cell crimping and disassembling machine (MTI, Korea). Electrolyte handling and device fabrication were carried out in a glove box with less than 1 ppm of moisture and oxygen. Electrochemical measurements of the siloxene SSC device such as CV at different scan rates, EIS analysis in the frequency range from 0.01 Hz to 100 kHz at an amplitude of 10 mV, and galvanostatic CD measurements in different current ranges were performed using an Autolab PGSTAT302N electrochemical workstation.

1.5 Electrochemical characterization

1.5.1 Determination of specific capacitance from CD profiles:

The specific capacitance of the siloxene SSC device was calculated from the CD profiles using the relation [4]:

\[ C_A = \frac{(I \times T_d)}{(A \times \Delta V)} \ldots (1) \]

\[ C_G = \frac{(I \times T_d)}{(M \times \Delta V)} \ldots (2) \]

Here “\( C_A \) and \( C_G \)” represents the specific areal capacitance (F/cm²) and gravimetric capacitance (F g⁻¹), “\( I \)” is the discharge current, “\( T_d \)” is the time required for discharge, “\( A \)” is the area of the electroactive material, “\( M \)” is the electroactive mass of siloxene in the SSC, and “\( \Delta V \)” is the potential window.
1.5.2 Determination of Energy and power density:

The energy and power density of the siloxene SSC device are calculated in terms of using the relations given below [5]:

\[ E = \frac{C \times \Delta V^2}{2} \]  \hspace{1cm} (3)

\[ P = \frac{E}{T_d} \]  \hspace{1cm} (4)

Here \( E \) and \( P \) are the energy and power density of the device, \( C \) is the specific capacitance, \( \Delta V \) is the potential window, and \( T_d \) is the discharge time.

1.5.3 Determination of specific capacitance from EIS analysis:

The specific capacitance of siloxene SSC device with respect to applied frequency obtained from the EIS analysis using the relation [6]:

\[ C = \frac{1}{2\pi f z'} \]  \hspace{1cm} (5)

Here \( C \) is the specific capacitance of the device, and \( f \) is the applied frequency, and \( z' \) is the imaginary part of impedance.

1.5.4 Determination of maximal power density from EIS analysis:

The maximal power density of siloxene SSC device was obtained from the EIS analysis using the relation [7]:

\[ P = \frac{V^2}{4\text{ESR}} \]  \hspace{1cm} (6)

Here \( V \) is the voltage window of the device, and \( \text{ESR} \) is the equivalent series resistance of the device.
Fig. S1. Digital photograph showing the formation of green coloured siloxene sheets via deintercalation of calcium from CaSi$_2$ (black colour) using ice cold HCl.
Fig. S2. X-ray diffraction pattern of CaSi$_2$.

The XRD pattern of the CaSi$_2$ (Fig. S2) shows the presence of sharp diffraction peaks corresponding to the JCPDS card no: 75-2192.
Fig. S3. Fourier transform infra red spectrum of CaSi$_2$.

Figure S3 shows the FT-IR spectrum of CaSi$_2$ shows the presence of vibration bands at 500, 875, 1115, 1501, and 1633, respectively are raised due to the vibrational modes of Ca and Si bonding in the CaSi$_2$. The observed vibration bands in the CaSi$_2$ are closely matched with the previous study on the FT-IR spectrum of CaSi$_2$ [8].
Fig. S4. X-ray photoelectron survey spectrum of CaSi$_2$ and siloxene sheets.

Figure S4 shows the typical X-ray photoelectron survey spectrum of CaSi$_2$ and siloxene sheets. The survey spectrum of CaSi$_2$ shows the presence of Ca, Si, C, and O groups whereas the siloxene sheets shows the presence of Si, C, and O groups. The absence of Ca states in the siloxene sheets suggested the removal of Ca from the CaSi$_2$ via the topochemical reaction.
Fig. S5. Typical core level spectrum of (a) Si 2p, and (b) Ca 2p states in CaSi\textsubscript{2}.

Figure S5 shows the core level X-ray photoelectron survey spectrum of Si 2p and Ca 2p states in CaSi\textsubscript{2} material. Figure S5 (A) represents the core level spectrum of Si 2p states in CaSi\textsubscript{2} which shows the presence of two peaks at binding energies 97.5 and 102.5 eV respectively. Figure S5 (B) represents the core level spectrum of Ca 2p states in CaSi\textsubscript{2} which shows the presence of two peaks at binding energies 347.5 and 350.5 eV respectively. The observed XPS spectrum of CaSi\textsubscript{2} is in good agreement with the reported work in literature [9].
Fig. S6. Comparative core-level spectrum of Si 2p states in CaSi$_2$ and siloxene sheets. The disappearance of peak observed at 98.5 eV suggested the delamination of Ca from CaSi$_2$ and the new band observed at 99 eV confirms the formation of siloxene sheets.

Figure S6 represents the core level spectrum of Si 2p states in CaSi$_2$ and siloxene sheets indicating the disappearance of peak at 97.5 eV in CaSi$_2$ and the formation of one small peak at 99.15 eV in siloxene sheets which correspond to the Si-Si binding energies and is in agreement with the previous study [10]. Further, the peak observed at 102.3 eV in the siloxene corresponds to the Si bonding with oxygen and hydroxyl groups [11].
Fig. S7. Morphological analysis of siloxene sheets. (A) low and (B) high magnification Field emission-scanning electron micrographs of siloxene sheets.
Fig. S8. (A) EDS spectrum of siloxene sheets and (B) shows the atomic weight (%) of O/Si is about 1.49 for the micrograph and mapping images of siloxene sheets given in shown in Figure 2 (A-C).
Fig. S9. Atomic force microscopic image of siloxene sheets.
Fig. S10. (A-C) Section analysis obtained from the atomic force microscopic image of siloxene sheets given in Fig. 2(F) and (D) section analysis of siloxene sheet given in Fig. S9.
The laser Raman spectrum of CaSi$_2$ is given in Fig. S11 represents presence of sharp Raman band at 515 cm$^{-1}$ and relatively weak band at 375 cm$^{-1}$ which corresponds to the bonding between Ca and Si in CaSi$_2$. In comparison with the Raman band of crystalline silicon (520 cm$^{-1}$) [12], the observed shift towards 515 cm$^{-1}$ is due to the CaSi$_2$. 

**Fig. S11. Laser Raman spectrum of CaSi$_2$.**
Fig. S12. N$_2$ adsorption–desorption isotherm of CaSi$_2$. 
Fig. S13. (A) N$_2$ adsorption–desorption isotherm and (B) pore size distribution of the prepared siloxene sheets.
Fig. S14. Microscopic characterization of siloxene coated stainless steel current collectors (A) Optical microscopic image, (B) 2D surface profile and (C) 3D surface profiles of the image of siloxene coated stainless steel current collectors indicating the thickness of the siloxene electrode is about ~7 µm.
Fig. S15. Ragone plot of siloxene SSC device in gravimetric metrics.
Table S1: Performance metrics of siloxene SSC device with reported SSCs using silicon based electrodes.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Electrode material</th>
<th>Electrolyte</th>
<th>Potential window (ΔV)</th>
<th>Specific capacitance</th>
<th>Energy density</th>
<th>Power density</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Silicon Nanowire</td>
<td>PYR$_{13}$TFSI</td>
<td>0 to 4 V</td>
<td>30 µF/cm$^2$</td>
<td>0.19 mJ/cm$^2$</td>
<td>1 to 2 mW/cm$^2$</td>
<td>[7]</td>
</tr>
<tr>
<td>2.</td>
<td>Silicon Nanotrees</td>
<td>EMI-TFSI</td>
<td>-2.5 to 1.5 V</td>
<td>3.8 mF/cm$^2$</td>
<td>2.8 mJ/cm$^2$</td>
<td>2 mW/cm$^2$</td>
<td>[19]</td>
</tr>
<tr>
<td>3.</td>
<td>Diamond coated Si NWs</td>
<td>PMPyrrTFSI</td>
<td>-2.5 to 1.5 V</td>
<td>105 µF/cm$^2$</td>
<td>84 µJ/cm$^2$</td>
<td>0.94 mW/cm$^2$</td>
<td>[20]</td>
</tr>
<tr>
<td>4.</td>
<td>Silicon nanowire coated RuO$_2$</td>
<td>PVA/H$_2$SO$_4$</td>
<td>-0.5 to 0.5 V</td>
<td>6.5 mF/cm$^2$</td>
<td>0.4 µWh/cm$^2$</td>
<td>0.17 mW/cm$^2$</td>
<td>[21]</td>
</tr>
<tr>
<td>5.</td>
<td>Silicon Nanotrees</td>
<td>EMI-TFSI</td>
<td>-1.3 to -0.3 V</td>
<td>58.3 µF/cm$^2$</td>
<td>0.262 mJ/cm$^2$</td>
<td>—</td>
<td>[22]</td>
</tr>
<tr>
<td>6.</td>
<td>Porous Si</td>
<td>PEO-EMIBF$_4$</td>
<td>0.0 to 0.65 V</td>
<td>3.5 mF/cm$^2$</td>
<td>0.17 µWh/cm$^2$</td>
<td>22 µW/cm$^2$</td>
<td>[23]</td>
</tr>
<tr>
<td>7.</td>
<td>Oxide coated Si</td>
<td>EMI-TFSI</td>
<td>-2.0 to 1.5 V</td>
<td>31 µF/cm$^2$</td>
<td>0.212 mJ/cm$^2$</td>
<td>0.472 mW/cm$^2$</td>
<td>[24]</td>
</tr>
<tr>
<td>8.</td>
<td>PEDOT coated Silicon nanowire</td>
<td>PYR$_{13}$TFSI</td>
<td>0 to 1.5 V</td>
<td>8.9 mF/cm$^2$</td>
<td>9 mJ/cm$^2$</td>
<td>0.8 mW/cm$^2$</td>
<td>[25]</td>
</tr>
<tr>
<td>9.</td>
<td>Carbon coated silicon nanowires</td>
<td>Na$_2$SO$_4$</td>
<td>0 to 0.7 V</td>
<td>817 µF/cm$^2$</td>
<td>—</td>
<td>—</td>
<td>[26]</td>
</tr>
<tr>
<td>10.</td>
<td>Graphene coated Silicon Nanowires</td>
<td>EMIM][N(Tf)$_2$</td>
<td>0 to 1.3 V</td>
<td>0.24 mF/cm$^2$</td>
<td>—</td>
<td>—</td>
<td>[27]</td>
</tr>
<tr>
<td>11.</td>
<td>SiC NWs on SiC film</td>
<td>KCl</td>
<td>-0.2 to 0.6 V</td>
<td>240 µF/cm$^2$</td>
<td>68 µJ/cm$^2$</td>
<td>4 µW/cm$^2$</td>
<td>[28]</td>
</tr>
<tr>
<td>12.</td>
<td>SiC coated Si NWs</td>
<td>KCl</td>
<td>-0.2 to 0.6 V</td>
<td>1.7 mF/cm$^2$</td>
<td>0.85 mJ/cm$^2$</td>
<td>~ 0.1 mW/cm$^2$</td>
<td>[29]</td>
</tr>
<tr>
<td>13.</td>
<td>SiC NW</td>
<td>KCl</td>
<td>0.0 to 0.6 V</td>
<td>23 mF/cm$^2$</td>
<td>2.3 mJ/cm$^2$</td>
<td>1.1 mW/cm$^2$</td>
<td>[30]</td>
</tr>
<tr>
<td>14.</td>
<td>Siloxene sheets</td>
<td>0.5 M TEABF$_4$</td>
<td>0 to 3.0 V</td>
<td>2.18 mF/cm$^2$</td>
<td>9.82 mJ/cm$^2$</td>
<td>4.03 mW/cm$^2$</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: 1. (–) indicates that the values are not provided in the corresponding references.
Table S2: Performance metrics (in areal) of siloxene SSC device with reported SSCs using 2D materials as electrodes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode material</th>
<th>Electrolyte</th>
<th>Potential window (AV)</th>
<th>Specific capacitance</th>
<th>Energy density</th>
<th>Power density</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Vertical Graphene-/Pt/Si</td>
<td>6 M KOH</td>
<td>-0.2 to 0.4 V</td>
<td>1.052 mF/cm²</td>
<td>4.88×10⁻⁴ Wh/m²</td>
<td>0.3 W/m²</td>
<td>[31]</td>
</tr>
<tr>
<td>2.</td>
<td>Planar Graphene Nanocup/Pt/Si</td>
<td>6 M KOH</td>
<td>-0.2 to 0.4 V</td>
<td>0.337 mF/cm²</td>
<td>1.83×10⁻⁴ Wh/m²</td>
<td>0.3 W/m²</td>
<td>[31]</td>
</tr>
<tr>
<td>3.</td>
<td>Ti₃C₂ MXene</td>
<td>PVA/H₂SO₄</td>
<td>0.0 to 0.6 V</td>
<td>6.2 mF/cm²</td>
<td>0.21 µWh/cm²</td>
<td>3.34 mW/cm²</td>
<td>[32]</td>
</tr>
<tr>
<td>4.</td>
<td>Edge-Oriented MoS₂</td>
<td>1 M LiOH</td>
<td>-0.8 to 0.8 V</td>
<td>14.5 mF/cm²</td>
<td>–</td>
<td>–</td>
<td>[33]</td>
</tr>
<tr>
<td>5.</td>
<td>SnSe NSs</td>
<td>PVA/H₂SO₄</td>
<td>-0.55 to 0.55 V</td>
<td>1.2 mF/cm²</td>
<td>–</td>
<td>–</td>
<td>[34]</td>
</tr>
<tr>
<td>6.</td>
<td>GeSe₂</td>
<td>PVA/H₂SO₄</td>
<td>0.0 to 0.6 V</td>
<td>0.2 mF/cm²</td>
<td>–</td>
<td>–</td>
<td>[35]</td>
</tr>
<tr>
<td>7.</td>
<td>Black Phosphorous</td>
<td>PVA-H₃PO₄</td>
<td>0.0 to 1.0 V</td>
<td>17.78 F/cm³</td>
<td>2.47 mWh/cm³</td>
<td>8.83 W/cm³</td>
<td>[36]</td>
</tr>
<tr>
<td>8.</td>
<td>WTe₂</td>
<td>PVA-H₃PO₄</td>
<td>0.0 to 1.0 V</td>
<td>74 F/cm³</td>
<td>0.01 Wh/cm³</td>
<td>83.6 W/cm³</td>
<td>[37]</td>
</tr>
<tr>
<td>9.</td>
<td>Graphene</td>
<td>H₂SO₄</td>
<td>0.0 to 1.0 V</td>
<td>11.1 mF/cm²</td>
<td>1.24 µWh/cm²</td>
<td>24.5 µW/cm²</td>
<td>[38]</td>
</tr>
<tr>
<td>10.</td>
<td>VS₂</td>
<td>BMIMBF₄</td>
<td>0.0 to 0.6 V</td>
<td>4.7 mF/cm²</td>
<td>–</td>
<td>–</td>
<td>[39]</td>
</tr>
<tr>
<td>11.</td>
<td>Exfoliated MoS₂</td>
<td>Et₄NBF₄</td>
<td>-1.0 V to 1.7 V</td>
<td>2.25 mF/cm²</td>
<td>–</td>
<td>–</td>
<td>[40]</td>
</tr>
<tr>
<td>12.</td>
<td>Exfoliated MoS₂</td>
<td>BMIM-PF₆</td>
<td>-2.0 V to 1.5 V</td>
<td>2.4 mF/cm²</td>
<td>–</td>
<td>–</td>
<td>[40]</td>
</tr>
<tr>
<td>13.</td>
<td>Siloxene nanosheets</td>
<td>0.5 M TEABF₄</td>
<td>0.0 to 3.0 V</td>
<td>2.18 mF/cm²</td>
<td>9.82 mJ cm⁻²</td>
<td>4.03 mW/cm²</td>
<td>This work</td>
</tr>
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</table>

Note: (–) indicates that the values are not provided in the corresponding references.
Table S3: Gravimetric performance metrics of siloxene SSC device with reported symmetric supercapacitors using 2D materials.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode material</th>
<th>Electrolyte</th>
<th>Potential window (ΔV)</th>
<th>Specific capacitance (F g(^{-1}))</th>
<th>Energy density Wh kg(^{-1})</th>
<th>Power density W kg(^{-1})</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Graphene</td>
<td>1M Na(_2)SO(_4)</td>
<td>0.0 to 1.0 V</td>
<td>3.13</td>
<td>—</td>
<td>—</td>
<td>[41]</td>
</tr>
<tr>
<td>2.</td>
<td>Exfoliated MoS(_2)</td>
<td>1M Na(_2)SO(_4)</td>
<td>0.0 to 1.0 V</td>
<td>2.68</td>
<td>—</td>
<td>—</td>
<td>[41]</td>
</tr>
<tr>
<td>3.</td>
<td>Exfoliated MoSe(_2)</td>
<td>1M Na(_2)SO(_4)</td>
<td>0.0 to 1.0 V</td>
<td>2.75</td>
<td>—</td>
<td>—</td>
<td>[42]</td>
</tr>
<tr>
<td>4.</td>
<td>Exfoliated TiS(_2)</td>
<td>1M Na(_2)SO(_4)</td>
<td>0.0 to 1.0 V</td>
<td>4.6</td>
<td>—</td>
<td>—</td>
<td>[42]</td>
</tr>
<tr>
<td>5.</td>
<td>Exfoliated WS(_2)</td>
<td>1M Na(_2)SO(_4)</td>
<td>0.0 to 1.0 V</td>
<td>3.5</td>
<td>—</td>
<td>—</td>
<td>[42]</td>
</tr>
<tr>
<td>6.</td>
<td>FeS Nanoplates</td>
<td>PVA-LiClO(_4)</td>
<td>0.0 to 2.0 V</td>
<td>4.62</td>
<td>2.56</td>
<td>726</td>
<td>[14]</td>
</tr>
<tr>
<td>7.</td>
<td>RuS(_2) Nanoparticles</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>0.0 to 0.8 V</td>
<td>17</td>
<td>1.51</td>
<td>40</td>
<td>[13]</td>
</tr>
<tr>
<td>8.</td>
<td>Ti(_2)CT(_x), MXene</td>
<td>PVA-H(_3)PO(_4)</td>
<td>0.0 to 1.0 V</td>
<td>4.9</td>
<td>0.335</td>
<td>700</td>
<td>[15]</td>
</tr>
<tr>
<td>9.</td>
<td>Ti(_2)CT(_x), 500 °C MXene</td>
<td>KOH</td>
<td>0.0 to 0.7 V</td>
<td>32.3</td>
<td>2.19</td>
<td>700</td>
<td>[16]</td>
</tr>
<tr>
<td>10.</td>
<td>Si Nanowires</td>
<td>BMI-TFSI</td>
<td>-0.6 to 1.0 V</td>
<td>0.7</td>
<td>0.23</td>
<td>0.65</td>
<td>[17,43]</td>
</tr>
<tr>
<td>11.</td>
<td>Siloxene nanosheets</td>
<td>0.5 M TEABF(_4)</td>
<td>0.0 to 3.0 V</td>
<td>4.06</td>
<td>5.08</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>

Note: (—) indicates that the values are not provided in the corresponding references.
References:


