DESCRIPTION KR102053782B1

SUPERCAPACITOR COMPRISING TWO DIMENSIONAL SILOXENE SHEETS AND PREPARATION METHOD OF THE SAME

[0001]

The present invention relates to a supercapacitor and a method for manufacturing the same, and more particularly, to a supercapacitor having improved capacity characteristics by applying a siloxane sheet as an electrode material, and a method for manufacturing the same.

[0003]

Increasing energy consumption demands and the fossil fuel depletion crisis have accelerated research into high - performance energy storage devices and delivery systems. Supercapacitors or electrochemical capacitors are attracting attention as ideal alternatives for energy storage devices due to their high power density, high discharge capacity ratio, and long lifespan. To increase the energy/power ratio of supercapacitors, attention is focused on the design and development of new electrode materials. In this regard, research is also being conducted to apply two - dimensional materials to next - generation energy storage devices.

[0004]

Since the advent of graphene sheets, several two - dimensional materials, including transition metal chalcogenides (MoS_2, VS_2, $MoSe_2$, TiS_2), M'Xenes, germanane, and phosphorene, have been developed and their energy storage properties are currently being studied.

[0005]

The fundamental charge - storage properties of these materials for supercapacitor and battery applications have been investigated over the past decade. However, questions are also being raised as to whether these materials for on - chip energy storage micro - devices can be applied to microelectronic devices, wireless sensor networks, and implantable biomedical devices, which have traditionally been applied to silicon - based materials.

[0006]

To address these issues, there is a need to develop alternative materials that can compete with current Si manufacturing technologies. Silicon - based materials for microcapacitors are thought to be an ideal choice for easier application in microelectronic device technology compared to conventional carbon - based materials [OLC (onion like carbon), CNT (carbon nanotube), graphene, carbide derived carbon, diamond foam].

[0007]

In addition, silicon - based materials such as silicon films, nanowires, nanoTRIS, porous silicon, morphous silicon, and their composites/blends are also in continuous demand for research for various electronic device applications including battery, supercapacitor or microcapacitor applications.

[0008]

Patent Publication No. 10 - 2016 - 0016385, published on February 15, 2016, Multilayer Ceramic Capacitor

[0009]

X. Zhang, L. Hou, A. Ciesielski, P. Samor μ, 2D Materials Beyond Graphene for High - Performance Energy Storage Applications, Adv. Energy Master. 6 (2016). doi:10.1002/aenm. 201600671

[0010]

The purpose of the present invention is to provide a supercapacitor having improved capacity characteristics and cyclic stability by applying a siloxane sheet as an electrode material, and a method for manufacturing the same.

[0012]

In order to achieve the above object, a method for manufacturing a supercapacitor according to one embodiment of the present invention includes a reaction step of immersing a precursor containing calcium silicide in an acid to dissolve calcium and obtain siloxane; a slurry preparation step of mixing the siloxane, a conductive carbon material, and a binder to prepare an electrode material slurry; and a sheet drying step of coating the electrode material slurry on a substrate and drying it to produce a siloxane sheet, thereby including a process for manufacturing an electrode including a siloxane sheet.

[0013]

The above electrode material slurry may contain 60 to 95 wt% of the siloxane.

[0014]

The above acid may be a strong acid having a temperature of 4 ° C or lower, or may be hydrochloric acid having a temperature of 4 ° C or lower.

[0015]

The above manufacturing method may further include a siloxane drying step between the above reaction step and the above slurry manufacturing step.

[0016]

The above siloxane drying step can be performed at a drying temperature of 60 to 90 ° C. for 6 to 20 hours.

[0017]

The above siloxane may be a product in which the (001) plane and (100) plane of silicon are developed.

[0018]

The above siloxane may have an O/Si atomic ratio of 1.3 to 1.45 as confirmed by XPS analysis.

[0019]

The above siloxane may include a Si plane of the Katsuki type and may include a hydroxyl group on its surface.

[0020]

The above siloxane may have a specific surface area of 30 to 90 m²g⁻¹ as measured using the N₂adsorption/desorption method.

[0021]

The above siloxane may have mesopores with an average pore size of 2 to 6 .

[0022]

The above manufacturing method may further include a separator arrangement step and an electrolyte injection step after the process of manufacturing the electrode.

[0023]

The above electrolyte may contain TEABF₄.

[0024]

According to another embodiment of the present invention, a supercapacitor comprises two or more electrodes containing an electrode material including siloxane, a conductive carbon material, and a binder; a separator positioned between the electrodes; and an electrolyte, wherein the siloxane has a developed (001) plane and (100) plane of silicon and includes a Si plane of the Katsuki type.

[0025]

The above siloxane may have a specific surface area of 30 to 90 m²g⁻¹ as measured using the N₂adsorption/desorption method.

[0026]

The above siloxane may have mesopores with an average pore size of 2 to 6 .

[0027]
The above supercapacitor may have an insertion capacitance.

[0028]
The above supercapacitor may have a capacitance of 1.9 to 2.4 mF cm^{- 2}.

[0030]
Hereinafter, the present invention will be described in more detail.

[0031]
Siloxane sheets, which are manufactured by removing calcium from calcium silicide, are two - dimensional linear structures containing interconnected Si chains with a surface having functional groups mainly composed of oxygen, hydrogen, and hydroxyl groups, making them interesting materials with direct bandgap properties. The inventors of the present invention successfully prepared a siloxane sheet (a two - dimensional (2D) silicon material) and investigated its energy storage properties through the fabrication of a symmetric supercapacitor (SSC) device of a CR2032 coin cell (battery) using a 0.5 M TEABF₄ electrolyte.

[0032]
X - ray diffraction analysis, X - ray photoelectron spectroscopy, high - resolution transmission electron microscopy and laser Raman mapping analyses revealed the formation of two - dimensional siloxane sheets with Si₆ rings functionalized with oxygen, hydroxyl and hydroxyl groups. Cyclic voltammetry studies of siloxane SSD devices confirmed the presence of pseudocapacitance from siloxane sheets through insertion/uninsertion phenomena. The galvanostatic charge - discharge profile showed a roughly symmetrical triangular curve with the highest specific capacitance (2.18 mF cm^{- 2}), high energy density (9.82 mJ cm^{- 2}) with good discharge - capacity ratio, and excellent cyclic stability (98% capacitance retention after 10,000 cycles). Moreover, the siloxane SSC device exhibited a maximum power density of 272.5 mW cm^{- 2} as obtained from electrochemical impedance spectroscopy, which is higher than that of other silicon and carbon - based supercapacitors,

highlighting its potential applications in energy storage fields.

[0033]

The inventors of the present invention, based on these experimental results and considering these experimental results of a 2D siloxane - based SSC device, completed the present invention believing that siloxane sheets would be promising electrode materials for next - generation energy storage devices.

In addition, since the planar Si structure with Si₆ ring can have various functional groups on the surface, the inventors of the present invention judged that the siloxane sheet is an excellent material applicable to supercapacitors.

[0034]

In order to achieve the above object, a method for manufacturing a supercapacitor according to one embodiment of the present invention includes a process for manufacturing an electrode including a siloxane sheet, including a reaction step; a slurry manufacturing step; and a sheet drying step.

[0035]

The above reaction step is a step of obtaining siloxane by immersing a precursor containing calcium silicide in acid to dissolve calcium.

[0036]

The above acid can be a strong acid having a temperature of 4 ° C or lower, and specifically, hydrochloric acid can be applied. It is advantageous for the reaction to proceed efficiently and obtain siloxane of a desired form by maintaining a temperature of 0 to 2 ° C while vigorously mixing under hydrochloric acid.

[0037]

The above reaction step can be carried out for 40 to 96 hours, or can be carried out for 60 to 80 hours, and such a transit reaction can be carried out efficiently and relatively completely.

[0038]

The progress of the reaction can be checked by checking the black color of calcium silicide changing to yellow color of siloxane. After the reaction is completed, the product can be recovered by washing with water and ultrasonic waves, separating it from water, and then drying it (siloxane drying step).

During this cleaning process, ultrasound can be performed at 15 to 25 kHz.

In addition, the above drying (siloxane drying step) can be performed at a drying temperature of 60 to 90 ° C. for 6 to 20 hours, and in this case, drying can be performed efficiently without damaging the siloxane and removing the reaction residue.

[0039]

The above slurry preparation step is a step of preparing an electrode material slurry by mixing siloxane, a conductive carbon material, and a binder.

[0040]

Siloxene manufactured by the method described above can be applied, and the properties of siloxene manufactured in this way are described in detail below.

[0041]

The conductive carbon material may include at least one selected from carbon black, graphene, and carbon nanotubes, and the binder may include at least one selected from the group consisting of PVDF (Polyvinylidene Fluoride), PTFE (Polytetrafluoroethylene), PVA (Polyvinyl Alcohol), and SBR (Styrene Butadiene).

[0042]

The above electrode material slurry may contain 60 to 95 wt% of the siloxane, and in this case, sufficient electrode active material may be contained to improve the performance of the capacitor.

[0043]

Specifically, the electrode material slurry may contain 60 to 95 wt% of the siloxane, 2 to 20 wt% of the conductive carbon material, and 2 to 20 wt% of the binder, and in this case, the performance of the capacitor may be further improved.

[0044]

More specifically, the electrode material slurry may contain 85 to 95 wt% of the siloxane, 2 to 8 wt% of the conductive carbon material, and 2 to 8 wt% of the binder, and in this case, the stability performance and capacity characteristics of the capacitor can be further improved.

[0045]

The above sheet drying step is a step of manufacturing a siloxane sheet by coating the electrode material slurry on a substrate and drying it.

[0046]

The above sheet drying step can be performed at a drying temperature of 60 to 90 ° C. for 6 to 20 hours, or at a drying temperature of 75 to 85 ° C. for 10 to 16 hours. In this case, the properties of the siloxane can be maintained while producing a siloxane sheet having properties such as strength required for the electrode of the capacitor.

[0047]

The method for manufacturing the above supercapacitor may further include a step of arranging a separator and a step of injecting an electrolyte after the process of manufacturing the electrode. At this time, the separator and the electrolyte may be applied if they are generally applied to supercapacitors, and for example, the electrolyte may include TEABF₄.

[0048]

The above siloxane has the characteristic that the (001) plane and (100) plane of silicon are developed. This is one of the characteristics that can vary depending on the reaction conditions or methods in siloxane that can be manufactured in various ways, and shows the characteristics of the siloxane of the present invention.

[0049]

The above siloxane may include a Si plane of the Katsuki type and may include a hydroxyl group on its surface. These features may contribute to the high capacity and charge-discharge stability of siloxane.

[0050]

It is preferable that the above siloxane have mesopores with porous characteristics, in which case the charge/discharge characteristics can be further improved.

In particular, the siloxane may have a specific surface area of 30 to 90 m²g⁻¹ as measured using the N₂adsorption-desorption method, and may have mesopores with an average pore size of 2 to 6 , and in this case, it may provide even better charge/discharge characteristics to the manufactured supercapacitor.

[0052]

According to another embodiment of the present invention, a supercapacitor comprises two or more electrodes containing an electrode material including siloxane, a conductive carbon material, and a binder; a separator positioned between the electrodes; and an electrolyte.

[0053]

The above siloxane has the characteristics described above, and specifically, the above siloxane may include a Si plane of the Katsuki type in which the (001) plane and (100) plane of silicon are developed.
The above siloxane may have an O/Si atomic ratio of 1.3 to 1.45, or may have an O/Si atomic ratio of 1.37 to 1.41, as confirmed by XPS analysis.
These O and Si may be homogeneously distributed within the siloxane sheet.

[0054]

In addition, the siloxane may have a specific surface area of 30 to 90 m²g⁻¹ as measured using the N₂adsorption-desorption method and mesopores with an average pore size of 2 to 6 .
When such siloxane is applied as an electrode material, it can provide excellent performance in terms of stability and electrostatic capacity, and the supercapacitor can have insertion electrostatic capacity.

[0055]

Specifically, the supercapacitor may have a capacitance of 1.9 to 2.4 mF cm⁻², which is higher compared to other silicon-based symmetric capacitor devices such as previously reported silicon nanowires (23 μF cm⁻²), silicon nanoTRIS (1.7 mF cm⁻²), 50 μm long silicon nanowires (0.44 mF cm⁻²), porous silicon (0.5 mF cm⁻²), and diamond-coated silicon nanowires (0.4 mF cm⁻²).

[0056]

In the present invention, the siloxane sheet prepared by removing calcium from calcium silicide becomes an interesting material having a two - dimensional linear structure and a direct bandgap including surface - linked Si chains having functional groups mainly composed of oxygen, hydrogen and hydroxyl groups.
It has been reported that the structure of siloxane sheets is greatly affected by experimental conditions such as reaction time, temperature, and solvent used.
The chemical structures of siloxenes proposed so far are partly Weiss - type structures (Si₆(OH)₃H₃, with optional Si - H and Si - OH bonds present on the surface of Si₆ rings) and partly Kautsky - type structures (Si₆O₃H, with Si₆ rings connected via Si - O - Si bridges).
Since the planar Si - Si structure with Si₆ rings can have various functional groups on the upper surface area, the inventors of the present invention anticipated that the siloxane sheet would be an optimal candidate for supercapacitor applications.

[0057]

In the experimental results of the present invention, the inventors of the present invention investigated in detail the supercapacitor characteristics of the siloxane sheet.
In conclusion, 2D siloxane sheets were successfully prepared via topochemical transformation reaction between CaSi₂ and cold HCl, and their high - ratio energy storage properties were demonstrated.
In addition, the supercapacitor characteristics of the siloxane sheet - based SSC device were confirmed, which showed a high specific capacitance (2.18 mF cm^{- 2}), high energy density (9.82 mJ cm^{- 2}), and good discharge - capacity ratio, which could be applied over a wide voltage range of 3.0 V.
272.5 The maximum power density of mW cm^{- 2} is higher than other silicon and carbon - based supercapacitors.
In addition, the siloxane SSC device showed excellent cyclic stability, with about 98% of the capacitance maintained even after more than 10,000 charge - discharge cycles. These experimental results of the present invention show that the electrode material of the present invention has high energy density, excellent charge - capacity ratio, and excellent cyclic stability when applied to a supercapacitor, and thus has great utility as a material for improving the characteristics of a supercapacitor.

[0059]

The supercapacitor of the present invention and its manufacturing method can provide an energy storage device, such as a supercapacitor, having an electrode material having excellent regulated capacity, high energy density with a high discharge capacity ratio, and excellent cyclic stability.

[0061]

FIG. 1 is a digital photograph showing the formation of green siloxane through insertion/deintercalation of calcium in $CaSi_2$ (black color) using (A) HCl, as applied in an embodiment of the present invention, (B) an X - ray diffraction pattern of a siloxane sheet, (C) a Fourier transform infrared spectrum of the siloxane sheet showing the presence of functional groups such as Si - H, Si - O, Si - OH, Si - O - Si, and $OSi_2{\equiv}Si-H$ on the surface, and a center level X - ray photoelectron spectrum of the siloxane sheet, graphs showing (D) Si 2p state and (E) O 1s state, respectively.

FIG. 2 shows the results of morphological analysis of a siloxane sheet manufactured in an embodiment of the present invention, observed using a field discharge scanning electron microscope. (A) is a low - magnification photograph, (B) is a high - magnification photograph, (C - E) are high - resolution transmission electron microscope photographs of siloxane observed at different magnifications, and (F) shows a diffraction pattern of the siloxane sheet showing an amorphous state.

FIG. 3 is a laser Raman spectrum of a silicon sheet showing functional groups attached to a (A) 2D silicon (Si_6) ring manufactured in an embodiment of the present invention.

Laser Raman mapping of the silicon sheet is shown in B – D, where (B) shows a peak position map of Si - O vibration observed at 495 cm^{-1}, (C) shows a peak position map of Si - Si vibration observed at 525 cm^{-1}, and (D) shows an intensity ratio map of I_{Si-O}/I_{Si-Si} peaks.

FIG. 4 shows the electrochemical analysis results of a silicon - based symmetric supercapacitor device (CR2032 coin cell) in 0.5 M $TEABF_4$ electrolyte tested in an embodiment of the present invention, where (A - C) show the cyclic voltammetry profiles of the silicon - based symmetric supercapacitor device measured at different scan rates ranging from 5 mV s^{-1} to 20 V s^{-1}, (D) shows the variation of a specific capacitance (region) with respect to the scan rate, and (E) shows the Nyquist plot of the siloxane supercapacitor device (the inset is a magnified graph of the high frequency region).

(F) represents the change in specific capacitance and phase angle in terms of applied frequency.

FIG. 5 is an experimental example using a device manufactured in an embodiment of the present invention, showing (A) galvanostatic charge - discharge profiles of a siloxane supercapacitor device measured at a continuous current of 0.5 mA, (B) charge - discharge profiles obtained by applying various currents, (C) a graph showing the effect of discharge current on a specific capacitance (area) of the siloxane supercapacitor device, and (D) a graph showing the discharge capacity ratio of the siloxane supercapacitor device.

FIG. 6 is a Ragone plot showing the power density versus energy density of (A) a siloxane supercapacitor device manufactured in an embodiment of the present invention, (B) a cycle stability test (results of more than 10,000 charge - discharge cycles) of a siloxane supercapacitor device showing better capacitance retention results, (C) and (D) are photographs showing the application of the supercapacitor device supplying power to 20 LEDs.

Figure 7 is an X - ray diffraction pattern of $CaSi_2$ applied in an embodiment of the present invention, showing the presence of a sharp diffraction peak corresponding to JCPDS card no: 75 - 2192.

Figure 8 is a Fourier transform infrared spectrum of $CaSi_2$ applied in an embodiment of the present invention, showing the presence of vibrational bands at 500, 875, 1115, 1501, and 1633 cm^{-1}, respectively.

FIG. 9 is an X - ray photoelectron survey spectrum of $CaSi_2$ and a siloxane sheet applied in one embodiment of the present invention, where the siloxane sheet shows Si, C, and O groups, while $CaSi_2$ shows the presence of Ca, Si, C, and O groups.

The absence of Ca in the siloxane sheet is due to the removal of Ca from $CaSi_2$ through topochemical reaction.

FIG. 10 shows the center level X - ray photoelectron survey spectra of (a) Si 2p and (b) Ca 2p states of $CaSi_2$ applied in an embodiment of the present invention, where (A) shows the presence of two peaks binding energies of 97.5 and 102.5 eV, respectively, and (B) shows the presence of two peaks binding energies of 347.5 and 350.5 eV, respectively.

FIG. 11 is a comparative center level spectrum of the Si 2p state in $CaSi_2$ and siloxane sheets applied in an embodiment of the present invention, where the disappearance of the peak at 97.5 eV in CaSi2 indicates delamination of Ca in $CaSi_2$, the formation of one small peak at 99.15 eV in the siloxane sheet corresponds to the Si - Si bonding energy, and the peak observed at 102.3 eV in siloxane corresponds to Si bonded with oxygen and hydroxyl groups.

Figure 12 is a laser Raman spectrum of $CaSi_2$ applied in an embodiment of the present invention, showing the presence of a sharp band corresponding to the connection between Ca and Si at 515 cm^{-1} and the presence of a relatively weak band at 375 cm^{-1}.

Figure 13 is an N_2 adsorption/desorption isotherm of $CaSi_2$ applied in an embodiment of the present invention.

Figure 14 shows (a) N_2 adsorption/desorption isotherm and (b) pore distribution of siloxane sheet measured in an embodiment of the present invention.

Figure 15 shows the cyclic voltammetric profiles (A - E) of the siloxane SSC device (measured at operating voltages of 1 to 3 V) measured in an embodiment of the present invention, and (F) the operating potential window for a specific capacitance.

FIG. 16 is a conceptual diagram explaining the process by which CaSi₂ manufactured in one embodiment of the present invention is transformed into a 2D siloxane sheet.

Figure 17 is a HR-TEM image of siloxane, where (A) is a photograph showing a sheet-shaped sample of less than 0.5 and less than 1 μm, and (B) and (C) are the results of electronic mapping of Si and oxygen atoms within the siloxane sheet.

Figure 18 shows the EDS spectrum and elemental analysis results of the siloxane sheet.

Figure 19 is an atomic force microscope (AFM) image of siloxane sheets dispersed on a mica substrate.

Figure 20 is an atomic force microscope (AFM) image of siloxane sheets dispersed on a mica substrate, with partial analysis results.

FIG. 21 is a diagram showing (A) an optical microscope image of a siloxane sheet manufactured in an experiment of the present invention, (B) a 2D surface profile showing that the thickness of the siloxane electrode is about 7 μm or less, and (C) a 3D surface profile.

[0062]

Hereinafter, embodiments of the present invention will be described in detail with reference to the attached drawings so that a person having ordinary skill in the art to which the present invention pertains can easily implement the invention.

However, the present invention may be implemented in various different forms and is not limited to the embodiments described herein.

[0064]

<Materials and Experimental Methods>

[0065]

Calcium silicide (CaSi₂) precursor and electrolyte (TEABF₄) were purchased from Alfa-Aesar, and hydrochloric acid (HCl) was purchased from Daejung Chemical.

Ultrasonic treatment was performed with a SONIC VCX 750 model (20 kHz, 750 W) using a direct immersion titanium tube.

[0066]

Siloxane sheets were prepared through the topochemical reaction of

CaSi₂ using cold hydrochloric acid. Briefly, 1 g of finely ground CaSi₂powder was immersed in HCl with vigorous stirring at 0 °C for four days. A color change from black CaSi₂ to yellow-green is observed, indicating that Ca dissolves slowly in HCl. After the reaction was completed, the green siloxane sheets were separated through a centrifugal separation process using acetone and water. The powder thus separated was immersed in 100 mL of water and then ultrasonicated for one hour. Finally, the green siloxane sheets were separated by centrifugation and dried at 80 °C for 12 hours.

[0067]

A Rigaku X-ray diffractometer system (operating at 40 KeV and 40 mA with Cu Kα radiation) was applied to investigate the purity and crystallinity of the prepared siloxen phase. The morphological observation of the surface of the siloxane sheet was performed using a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL Instruments). The morphology of the siloxane sheets was captured using a CCD 4k x 4k camera (Ultra Scan 400SP, gatan cop.) using high-resolution transmission electron microscopy (HRTEM; Jem 2011, Jeol cop.) was observed. The presence of functional groups in the siloxane sheets was investigated using Fourier transform infrared (FT-IR) spectroscopy performed on a Thermo scientific FT-IR spectrometer. Siloxane was mixed with KBr and compressed into transparent tablets for measurements, with pure KBr used as background. The chemical composition and state of the elements present in the outermost layer of the siloxane sheet were observed by X-ray photoelectron spectroscopy (XPS) using ESCA-2000, VG Microtech Ltd. 1486.6 A monochromatic X-ray source of eV (aluminium anode) and 14 kV was used to scan the sample surface. A high-discharge X-ray source with an aluminum anode was used to generate X-rays, and a quartz crystal monochromator was used to scan the samples. A LabRam HR Evolution Raman spectrometer (Horiba Jobin-Yvon, France) was used for Raman spectral measurements of the samples. The Raman system uses an Ar⁺ion laser operating at 10 mW with an excitation wavelength of 514 nm; a point acquisition time of 10 s was used to acquire the data.

Raman mapping of siloxane sheets was performed using LabSpec (Ver.

6.2) was analyzed using software.

Intensity ratio maps and peak distribution maps were used to analyze the structure of siloxane.

The adsorption–desorption isotherms of CaSi₂ and N₂ siloxane sheets were measured at 77 K using a NOVA 2000 system (Quantachrome, USA).

Additionally, the pore distribution was calculated using the Horvath-Kawazoe (HK) method.

First, for the preparation of the working electrode, a mixture was obtained in the form of a uniform slurry using siloxane powder, carbon black and PVDF ground in a ratio of (90:5:5) under NMP (solvent) using a manno mortar.

Afterwards, the slurry-type mixture was spin-coated on a stainless steel substrate at a speed of 200 rpm and dried at 80 ° C for 12 hours.

A symmetrical supercapacitor based on siloxane was fabricated as a coin cell (CR2032) using a siloxane-coated stainless steel substrate and Celguard membrane-separated electrodes, and 0.5 M TEABF₄ as an electrolyte.

The fabricated device was crimped using an Electric Coin Cell Crimping and Disassembling Machine (MTI Korea).

Electrolyte and coin cell device fabrication was performed inside a glove box with a humidity of 1 ppm and below air.

Electrochemical measurements such as cyclic voltammetry (CV) at various scan rates, electrochemical impedance spectroscopy (EIS) analysis (frequency from 0.01 Hz to 100 kHz and amplitude of 10 mV), and galvanostatic charge and discharge (CD) measurements at different current amplitudes for the siloxane-based SSC devices were performed using an Autolab PGSTAT302N electrochemical terminal.

[0069]

<Experimental Results>

[0070]

Siloxane nanosheets were obtained by topochemical reaction of CaSi₂ into two-dimensional siloxane sheets using cold HCl followed by sonication for more than four days.

Figure 1 (A) shows a digital photograph of CaSi₂ powder and the manufactured siloxane sheet.

The color change from black to green indicates that calcium was removed from CaSi₂ by HCl during the formation of siloxane sheets.

Specifically, referring to FIG. 16, (A) shows the structure of CaSi₂,

(B) explains how it changes into a siloxane sheet through a topochemical change, and (C) explains the structure of the siloxane sheet produced as a result.

640 That is, it explains the topotactic transformation of layered $CaSi_2$ into two-dimensional siloxane sheets using ice-cold hydrochloric acid.

644 The slow dissolution of calcium in the hydrochloric acid solution generates hydrogen gas, which activates the hydroxyl groups of the siloxane sheets during the reaction, and this is visualized as the black sample changing to green during the reaction.

647 To confirm the structure of the siloxane sheet, the X-ray diffraction analysis results of the manufactured siloxane sheet were observed and compared with those of $CaSi_2$ (see Fig. 7).

650 The XRD pattern of $CaSi_2$ shows the presence of sharp diffraction peaks that match well with JCPDS card No: 75-2192, and a significant change in the XRD pattern of the siloxane sheet was observed after the topochemical reaction (see Fig. 1 (B)).

654 Specifically, (i) the diffraction peak corresponding to $CaSi_2$ almost completely disappeared.

656 And (ii) two new broad peaks were observed at $2\theta = 13.5°$ and 26° in the XRD pattern of the siloxane sheets corresponding to the (001) and (100) planes of 2D silicon obtained from $CaSi_2$ with a hexagonal unit cell.

[0071]

662 The presence of functional groups in the siloxane sheet was confirmed by the Fourier transform infrared spectrum as shown in Fig. 1 (C).

664 Compared with the FT-IR spectrum of $CaSi_2$, the FT-IR spectrum of the siloxane sheet shows sharp and broad bands, respectively (see Fig. 8).

666 452, 867, 1034, 1639, And the bands observed at 2140 cm^{-1} correspond to the vibrations of ν(Si-Si), ν(Si-H), ν(Si-O-Si), ν(Si-OH), and $\nu(OSi_2{\equiv}Si\text{-}H)$, respectively. The presence of $\nu(OSi_2{\equiv}Si\text{-}H)$ suggests the presence of Si planes with Kautsky-type mainly composed of Si_6 rings interconnected through Si-O-Si bridges. The broad band observed at 3400 cm^{-1} is due to the hydroxyl groups present in siloxenes, which arise from the oxidation and hydroxylation occurring during the topochemical reaction.

[0072]

677 The changes in elements present in siloxane were compared with $CaSi_2$ using X-ray photoelectron spectroscopy.

679 The comparative XPS spectra of $CaSi_2$ and siloxane sheets showing the presence of Ca and Si components in the XPS spectrum of $CaSi_2$ and the disappearance of Ca component in the spectrum of siloxane after

topochemical reaction are shown in Fig. 9. The central level spectra of Ca and Si present in CaSi₂ are shown in Fig. 10. Their binding energies are consistent with those reported in previous studies.

[0073]

Figure 1(D) shows the center level spectrum of the Si 2p and O 1s states of the siloxane sheet, showing the presence of two peaks at 99 and 103 eV, respectively. The former peak corresponds to the Si 2p state of Si - Si bonded in siloxane, and the latter peak corresponds to the oxygenation and hydrogenation of the siloxane sheets. Compared with the Si 2p states of CaSi₂ and siloxane (see Fig. 11), the peak observed at 97 eV corresponding to Ca - Si bonded to CaSi₂ disappeared, and the formation of a new peak around 99 eV confirmed the formation of 2D siloxane sheets via topochemical reaction. Figure 1(E) shows the O 1s spectrum showing the presence of a broad peak around 531 eV associated with functionalized oxygen and hydroxyl groups of the siloxane sheet. The O/Si atomic ratio of the siloxane sheet revealed in the XPS analysis was 1.39.

[0074]

The surface morphology of the siloxane sheet was analyzed by FE - SEM and HR - TEM as shown in Fig. 2. FE - SEM images shown in Fig. 2 (A) and (B) showed the sheet structure of siloxane with folded and crumpled edges. Additionally, as shown in (C) to (E) of Fig. 2, HR - TEM images at different magnifications showed the presence of siloxane sheets of various layers. High - magnification images shown in Fig. 2(D) and (E) show the structure of several very thin layers of siloxane sheets, and the SAED pattern shown in Fig. 2(F) shows that the siloxane sheets are amorphous and composed of several layers rather than a single layer. Figure 17 is a HR - TEM image of siloxane, where (A) is a photograph showing a sheet - shaped sample of less than 0.5 and less than 1 μm, and (B) and (C) are the results of electronic mapping of Si and oxygen atoms within the siloxane sheet. Figure 18 shows the EDS spectrum and elemental analysis results of the siloxane sheet. It was shown that silicon and oxygen atoms were homogeneously distributed in the siloxane sheet with an oxygen/silicon atom ratio of approximately 1.49. Figures 19 and 20 show atomic force microscopy (AFM) images of siloxane sheets scattered on a mica substrate and the results of their partial analysis, confirming that they are thin sheets of 7 to 20 nm.

[0075]

Laser Raman spectroscopy and mapping are among the important tools for understanding the role of functionalization, crystal properties, defects, etc. in two-dimensional materials such as graphene, transition element chalcogenides, etc. The Raman bands observed in the siloxane sheet, as shown in Fig. 3(A), show the presence of Si-Si, Si-O, and Si-H groups. Compared to the Raman spectrum of $CaSi_2$, the sharp band observed at 515 cm^{-1} is broadened and divided into two bands at 495 and 525 cm^{-1} due to the vibrations from the Si-O (495 cm^{-1}) and Si-Si (520 cm^{-1}) bonds (see Fig. 12). Another minor band observed at 375 cm^{-1} is also due to the vibration of Si-Si. Additionally, the bands observed at 640 and 740 cm^{-1} are due to Si-H vibrations.

[0076]

To understand the state of Si-O and Si-Si vibration modes in more detail, Raman mapping analysis was performed, and the maximum position maps of Si-O and Si-Si vibrations are shown in Fig. 3 (B) and (C), respectively. The Si-O band positions varied from 495 to 505 cm^{-1} and were shown in red (495 cm^{-1}), rose (500 cm^{-1}), and yellow (505 cm^{-1}) on the map (see Fig. 3 (B)). The peak position map of Si-Si vibrations shows the presence of yellow, rose, red and green colors corresponding to positions around 525, 521, 517 and 515 cm^{-1} in the measured region, respectively (see Fig. 3(C)).

[0077]

To understand the interconnection of Si-NER116_ rings and Si-O in the siloxane sheet, the Si-O/Si-Si intensity ratio map was investigated, and the results are shown in Fig. 3(D). The Si-O/Si-Si intensity ratio map shows a wide range of intensity ratios from 0.3 to nearly 2.0, indicating that Si-O is hetero-linked onto the Si_6 ring of siloxane.

[0078]

The removal of calcium and transformation into siloxane in $CaSi_2$ was confirmed using surface area analysis.

771 The surface area and pore size of the siloxane sheet were analyzed by the N₂adsorption/desorption analysis method and compared with the results of CaSi₂ presented in Fig. 13.
771 The surface area of CaSi₂ was measured as 2.12 m²g⁻¹, and no large pores were observed.

[0079]
779 The topological chemical reaction results in the formation of pores and an increase in the surface area of the siloxane sheets, as confirmed by the N₂adsorption/desorption isotherm as shown in Fig. 14(A).
782 The isotherm observed in (A) of Fig. 14 belongs to a type IV curve (IUPAC standard classification).
784 And this result implies the existence of mesopores.

[0080]
788 The surface area of the siloxane sheet was measured to be 59.72 m²g⁻¹, and the average pore size was approximately 4.0 , respectively.
792 The obtained high surface area of the siloxane sheet with mesopores is advantageous for obtaining better electrochemical properties.

[0082]
797 The electrochemical capacitance characteristics of the siloxane sheets were analyzed after fabrication of symmetric supercapacitors in the form of coin cells CR2032 using 0.5 M TEABF₄ electrolyte.
800 To measure the applied operating potential window of a siloxene symmetric supercapacitor (SSC) device, cyclic voltammetric (CV) analysis was performed at different operating potential windows at a scan rate of 400 mV s⁻¹, and the results are presented in Fig. 15(A) to (E), showing that the SSSC device can be operated in a potential window of 3 V.
805 Additionally, the specific electrostatic capacitance value for the operating potential window shown in (F) of Fig. 15 showed a linear increase form that increased in proportion to the potential window value.
808 This demonstrates that the siloxane SSC device has good electrochemical stability.

[0083]
812 To understand the state of charge storage in the siloxane SSC, CV analysis was

measured at different scan rates (5 mV s⁻¹ to 20 V s⁻¹) and the results are shown in Fig. 4(A) to (C).

814 The CV profile measured at scan rates of 5 to 100 mVs⁻¹ is shown in Fig. 4(A) and shows a pseudo-rectangular curve with the presence of a small redox peak.

819 The observed redox peaks are thought to be due to the intercalation-deintercalation of electrolyte ions into the porous silicon and siloxane sheets similar to those of Ti₃C₂M'Xenes.

[0084]

825 As shown in (B) and (C) of Figure 4, increasing the scan rate from 100 mV s⁻¹ to 20 V s⁻¹ resulted in an increase in the current range.

828 And the redox peak was not observed at high scan rates.

829 The rectangular shape of the CV profile was maintained even at high scan rates exceeding 200 mV/s, demonstrating the better performance of the siloxane SSC device.

[0085]

835 Fig. 4(D) shows the representation of a specific electrostatic capacitance versus the scan ratio.

837 This showed that the siloxane device possessed a specific capacitance of about 4.91 mF cm⁻² at a scan rate of 5 mV s⁻¹.

839 Additionally, the siloxane device delivered a specific capacitance of about 2.12 mF cm⁻², which increased with scan rate by about 20 times.

[0086]

844 20 At a very high scan rate of V s⁻¹, the device was found to have a specific capacitance of about 219 μF cm⁻², indicating good rate capability of the material applied in the siloxane device.

[0087]

850 Electrochemical impedance spectroscopy data were applied to understand the charge-storage behavior in the siloxane SSC device, and the results were analyzed by Nyquis and Bode plots.

853 The Nyquis plot shown in Fig. 4(E) shows the presence of three parts, i.e., typical low-frequency, intermediate-frequency and high-frequency parts, corresponding to the synchronous charging, asynchronous charging and non-charging that occur simultaneously in the siloxane SSC device.

[0088]

In the low frequency region, the vertical lines almost parallel to the Y-axis show the capacitive behavior of the siloxane SSC device. The intermediate frequency region with a slope of 45 ° is influenced by the presence of pores with time constants over a wide range, which causes the asynchronous charging behavior of the siloxane SSC device. In the high-frequency region, well-defined semicircular arcs were observed due to the resistance between the electrolyte and the electrode material. The equivalent series resistance (ESR) of the Siloxane SSC device was found to be 4.379 Ω, and it exhibited a maximum power density of approximately 272.5 mW cm⁻².

[0089]

The obtained maximum power density of the siloxane-based SSC device is higher compared to the reported maximum power densities of other silicon-based supercapacitors, such as silicon nanowire-based ultracapacitors (182 mW cm⁻²), 10 μm long silicon nanowires (1.6 mW cm⁻²), silicon nanoTRIS (235 mW cm⁻²), silicon-based carbon-based ultracapacitors (34.4 mW cm⁻²), and onion-like carbon-based ultracapacitors (240 mW cm⁻²).

[0090]

These results of the present invention demonstrate the utility of siloxane-based devices with high power density as a suitable alternative to carbon-based applications for microelectronic devices.

[0091]

The effect of frequency on the capacitance of the siloxane SSC device is shown in Fig. 4(F), and the specific capacitance of the siloxane SSC device was found to decrease with increasing frequency, and in the high frequency part, the siloxane SSC device operates similarly to a resistor.

1

.33 The maximum specific capacitance of mF cm⁻² was obtained at a low frequency of about 0.01 Hz.

[0092]

As shown in (F) of Fig. 4, the Bode phase angle plot showed that the phase angle in the tail (low frequency region) was approximately -65°. The phase angle of an ideal capacitor is closer to -90°, and that of a pseudocapacitance is closer to -45°. The phase angle of about -65° in the siloxane SSC device showed the presence of insertion capacitance in the siloxane. Additionally, the capacitor response frequency (f_o) at a phase angle of -45° was observed at 13.89 Hz and the relaxation time of the siloxane SSC device was calculated to be 71 ms, which is comparable to the recorded values of silicon and carbon-based supercapacitors. These values are comparable to the performance of silicon-based or carbon-based supercapacitors.

[0093]

0.5

The galvanostatic CD profile of the siloxane SSC device measured at a constant current of 10 mA is shown in Fig. 5(A) and shows a pseudo-symmetric charge-discharge behavior. Figure 5(B) shows the CD profiles of the siloxane SSC device measured at different currents. Specifically. Symmetric profiles were obtained at high currents, while nearly symmetric profiles were obtained at low scan rates, corresponding to those observed at low powers, consistent with the CV profiles.

[0094]

Figure 5(C) shows the effect of discharge power at a specific capacitance of the siloxane SSC device. This graph shows that the specific capacitance increases with the corresponding decrease in discharge power and that the Siloxane SSC device delivers a specific capacitance of about 2.18 mF cm⁻² at a current of about 0.25 mA.

[0095]

The specific capacitance obtained from the siloxane SSC device is higher compared to other silicon-based symmetric capacitor devices, such as, for example, silicon nanowires (23 μF cm⁻²), silicon nanotrisses (1.7 mF cm<sup>-

2</sup>), 50 μm long silicon nanowires (0.44 mF cm⁻²), porous silicon (0.5 mF cm⁻²), and diamond-coated silicon nanowires (0.4 mF cm⁻²).

[0096]

952 High discharge capacity ratio is one of the most important features of supercapacitors.
954 Figure 5 (D) shows the discharge capacity ratio of the siloxane SSC device.
955 Referring to Fig. 5 (D), it shows stable circulation at all currents (0.5 to 10 mA), and has reversible characteristics with good retention when the circulation is changed from low power to high power and vice versa.

[0097]

961 The present invention demonstrates that a siloxane SSC device can transmit energy.
962 Among the key features of supercapacitors, energy density, power density and cyclic stability at various load levels are important features that enable practical application of supercapacitor devices.

[0098]

968 The energy and power densities of the Siloxane SSC device were measured from CD profiles.
970 And the Ragone diagram is shown in Fig. 6 (A).
971 This shows that the siloxane SSC device delivered an energy density of about 9.82 mJ cm⁻² obtained at a constant current of 0.25 mA with a corresponding power density of 0.2 mW cm⁻².

[0099]

977 The energy density of the Siloxane SSC device decreased from 9.82 to 3.22 mJ cm⁻² when the power density increased from 0.2 to 4.03 mW cm⁻² and the galvanostatic discharge current density increased from 0.25 to 5 mA.

[0100]

984 The power density values of the Siloxane SSD device are compared with other silicon-based supercapacitor systems.
986 The siloxane SSD system shows high power densities compared to other supercapacitors based on Si nanowires (1 - 2 mW cm⁻²), highly

doped Si nanowires (1.6 mW cm⁻²), polypyrrole (PPy) (0.56 mW cm⁻²), PEDOT-coated Si nanowires (0.8 mW cm⁻²), MnO₂ nanoflakes on Si nanowires (1 mW cm⁻²), and ruthenium oxide-coated Si nanowires (0.17 mW cm⁻²), respectively.

[0101]

Figure 6(B) shows the cycle stability of the siloxane SSC device after more than 10,000 charge-discharge cycles at a current of 2 mA. The Siloxane SSC device demonstrated approximately 98% capacitance retention and demonstrated excellent cycling stability and excellent electrochemical reversibility.

[0102]

Figures 6(C) and (D) show that the stored energy of the fabricated siloxane SSC device charged to 3 V was transferred to 20 green LEDs that were lit for almost 15 seconds, demonstrating practical application.

[0103]

These results demonstrate the potential use of the siloxane SSC of the present invention in next-generation energy storage applications. The excellent performance of Siloxane SSC with these excellent properties is thought to be due to the following factors.

[0104]

(i) The conductive hexagonal silicon framework of the siloxane sheet enables both ion release and electron transfer on the surface of the sheet.

[0105]

(ii) The wide interlayer space between each layer resulting from the presence of functional groups provides an active area for ion insertion/removal reactions.

[0106]

(iii) The large surface area and wide pore distribution of the siloxane sheet allow ions to move as quickly as possible through the surface of the sheet.

[0107]

(iv) The use of TEABF4 as an electrolyte in SSC provides a wide OPW, which is important for increasing the energy density of the supercapacitor.

[0109]

Although the preferred embodiments of the present invention have been described in detail above, the scope of the present invention is not limited thereto, and various modifications and improvements made by those skilled in the art using the basic concept of the present invention defined in the following claims also fall within the scope of the present invention.