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

Journal:	*Journal of Materials Chemistry A*
Manuscript ID:	TA-COM-01-2015-000321.R2
Article Type:	Communication
Date Submitted by the Author:	23-Mar-2015
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Synthesis of a calcium-bridged siloxene by a solid state reaction for optical and electrochemical properties

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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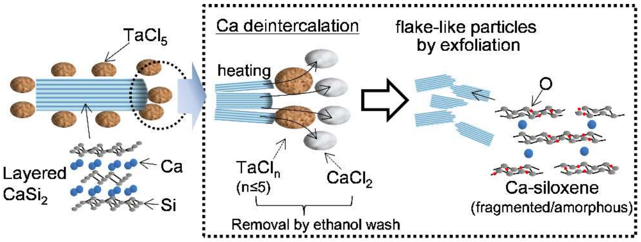
A Ca-bridged siloxene (Ca-siloxene) resulting from the deintercalation of Ca from $CaSi_2$ was synthesized via a solid state reaction with ethanol wash using $TaCl_5$. The presence of fragmented, two-dimensional siloxene planes with Ca bridging was confirmed. The Ca-siloxene exhibited tunable optical properties, as well as stable Li storage performance by Ca bridging.

Silicon is a chemically-stable, bio-inert and readily available element, and silicon-based compounds have attracted much attention due to their characteristic optical and electrochemical properties[1,2] for energy conversion and storage. These properties are known to be tunable based on variations in the structure and composition of the compounds. As an example, crystalline Si (c-Si) is not suitable for light emission applications as the result of its indirect narrow bandgap of 1.1 eV, and so there have been investigations with regard to generating direct bandgaps in silicon-based materials such as amorphous Si (a-Si)[3,4] and polysilane.[5,6] In addition, nanoscale materials such as porous Si[7,8], Si nanocrystals[9,10] and Si nanosheets[11] show promise, since they may exhibit unique optical properties resulting from the quasi-direct bandgaps brought about by their small sizes. These Si-based materials have also been investigated as to their electrochemical applications, especially for an anode material in Li ion batteries, since their characteristic structures tend to resist structural decomposition during charge/discharge cycling.[2,12]

Siloxene is an interesting material with a direct bandgap resulting from the presence of two-dimensional (2D) Si-based planes. Typical siloxene formulae are $Si_6(OH)_3H_3$, in which alternating Si-H and Si-OH bonds are present around Si_6 rings in a Weiss-type structure,[14-16] and $Si_6O_3H_6$, in which Si_6 rings are connected through Si-O-Si bridges in a Kautsky-type structure[16,17] (Fig. S1). Siloxene is typically synthesized using a solution method with $CaSi_2$, which is itself composed of alternating Si and Ca layers, and aqueous HCl, at or below room temperature.[14-17] During this synthesis, Ca atoms are completely deintercalated due to the highly acidic environment and substituted with H, OH or O linkages during the washing and drying processes, generating stacked Si-based planes. As a result of this formation process, it is difficult to control both the composition of the finished product, including the extent of Ca deintercalation, and the structure, such as the presence of bridging or doping with other atoms.



Scheme 1. The solid state reaction employed for Ca-siloxene synthesis.

Herein we report a convenient method for the synthesis of calcium-bridged siloxene (Ca-siloxene), applying a solid state reaction with ethanol wash. In a typical solid-state metathesis reaction, a starting material consisting of layered $CaSi_2$ reacts with metal chlorides, resulting in the generation of a metal silicide due to the formation of the stable compound $CaCl_2$ as the driving force for the reaction.[18] The reaction of $CaSi_2$ and $FeCl_2$, for example, forms Fe-silicides as the result of the deintercalation of Ca and the subsequent substitution with Fe.[18] In this process, the $CaCl_2$ byproduct is normally removed by washing with polar solvents. However, in our reaction, $TaCl_5$ (with a melting point of 221 °C) was employed as the chloride source in conjunction with the use of low temperature heating at 215 °C. This prevented the formation of Ta-silicide, such that only the deintercalation of Ca from $CaSi_2$ proceeded without any substitution by Ta (eqn. 1).

$$CaSi_2 + mTaCl_5 \rightarrow Ca_xSi_2 + (1-x)CaCl_2 + mTaCl_n\ (x < 1,\ n < 5) \text{ - (1)}$$

Then, Ca-siloxene may form with the aid of trace amount of H_2O in ethanol and HCl derived from tantalum chloride species (Scheme 1), in an analogous to siloxene synthesis[16,17] (eqn. 2).

$Ca_xSi_2 + 2yHCl + yH_2O \rightarrow Ca_{x-y}Si_2O_yH_{2y} + yCaCl_2 + yH_2$ ($y < x$) - (2)

The extent to which Ca is deintercalated from the $CaSi_2$ is mainly controlled by varying the $TaCl_5$ concentration, thus maintaining partial Ca-bridging between the fragmented Si-based layers, potentially imparting an intermediate or hybrid character to the product; partway between $CaSi_2$ and siloxene with respect to both structure and properties for energy conversion and storage. In this report, we demonstrate the characterization of synthesized materials with optical properties and the application to an anode material in Li ion batteries utilizing the structural characteristics.

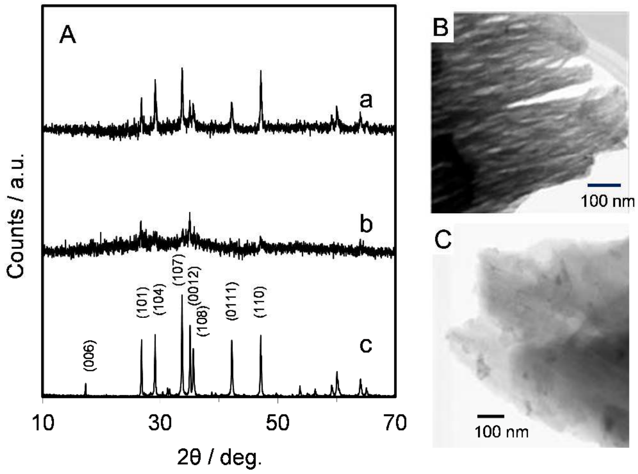


Fig. 1 (A) XRD patterns of (a) CS0.25, (b) CS2.5, and (c) $CaSi_2$, and STEM images of (B) CS2.5 and (C) CS0.25.

Samples were synthesized using Cl_2/Ca molar ratios of 0.25 and 2.5 (denoted as CS0.25 and CS2.5, respectively) at 215 °C for 5 h under Ar. Dark brown powders were obtained after washing with ethanol and drying under vacuum. Fig. 1(A) shows the powder X-ray diffraction (XRD) patterns of both types of samples. Broad peaks derived from $CaSi_2$ are dominant and no other peaks appear with the increase in the Cl_2/Ca ratio. The broad peaks are primarily located in the region of 25 to 40°, and are different from the peaks typically generated by SiO_2 or a-Si, suggesting that the synthesized samples had amorphous structures, likely due to fragmentation of layered $CaSi_2$ by exfoliation. The in-plane reflection peak was not clearly observed probably due to its fragmented and amorphous structure. As noted, XRD peaks originating from other materials were not observed and therefore it is evident that any residual $CaCl_2$ and tantalum chloride species were removed by the washing step.

The scanning transmission electron microscope (STEM) image of CS2.5 presented as Fig. 1(B) indicates that the majority of the primary particles had nano-sized, flake-like structures with a thickness close to 15 nm, and that these aggregated to form secondary particles. A N_2 adsorption-desorption isotherm also demonstrated a typical IUPAC H3-type hysteresis loop with a slit-like structure (Fig. S2). In contrast, the CS0.25 was composed of relatively large bulk particles without the flake-like structure of the CS2.5 (Fig. 1(C)). Based on these results, it appears that the primary particles were gradually reduced in size concurrent with the formation of flake-like particles as the Cl_2/Ca ratio was increased, due to the exfoliation of the original layered structure by Ca-deintercalation.

The average composition of CS0.25 as determined by electron dispersive X-ray analysis was Ca:Si:O = 1.8:6:1.5, indicating a partially Ca deintercalated and oxidized intermediate structure. The Si bonds remaining after Ca deintercalation appear to have been partially combined with O or H atoms through the washing steps. The CS2.5 exhibited a significantly different composition in which Ca:Si:O = 0.3:6:2.8, showing that it is possible to control the extent of Ca deintercalation by varying the Cl_2/Ca ratio.

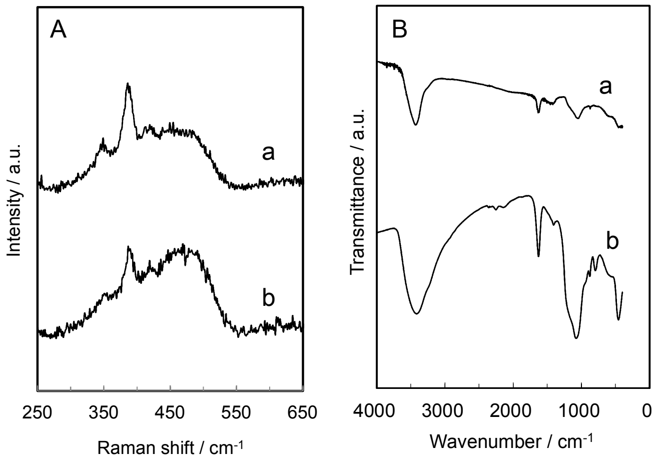


Fig. 2 (A) Raman spectra and (B) FT-IR spectra of (a) CS0.25 and (b) CS2.5.

Raman spectra of samples showed broad peaks in the range of 300 to 500 cm^{-1} due to Si-Si vibrations, providing evidence for the presence of Si-based planar structures (Fig. 2(A)). In particular, a broad peak at approximately 470 cm^{-1} derived from fragmented Si_6 rings in Si-based planes and a sharp peak at 380 cm^{-1} resulting from Si-based planes were both clearly observed,[19] supporting the presence of a Si-based planar structure.

Absorption bands attributed to the siloxene structure were present in the Fourier transform infrared (FTIR) spectrum of CS2.5 (Fig. 2(B)). Characteristic peaks are seen at 2150, 1060 and 1180 (shoulder), 610 (shoulder) and 460 cm^{-1}, corresponding to the $\nu(OSi_2{\equiv}Si\text{-}H)$, $\nu(Si\text{-}O\text{-}Si)$, $\delta(Si\text{-}H)$ and $\delta(Si\text{-}O\text{-}Si)$ modes[6,16,19,20,21]. The observation that the spectrum exhibits the $\nu(OSi_2{\equiv}Si\text{-}H)$ mode but not the $\nu(Si_3{\equiv}Si\text{-}H)$ and $\nu(O_2Si{\equiv}Si\text{-}H)$ modes suggests the presence of Si planes with a Kautsky-type siloxene structure, composed primarily of Si_6 rings connected through Si-O-Si bridges (Fig. S1). In addition, the absence of the $\nu(O_2Si{\equiv}Si\text{-}H)$ mode implies that Ca bridging is the only interlayer linkage and that interlayer Si-O-Si bonding is not present. Therefore, it is believed that the remaining interlayer Ca atoms formed bridges between fragmented siloxene layers, generating the siloxene in an amorphous state. Judging from the presence of the band at 2250 cm^{-1}, attributed to the $\nu(O_3{\equiv}Si\text{-}H)$ mode, and broad bands around 3400 cm^{-1} due to the $\nu(\text{-}OH)$ mode, the edges and the majority of the surface area of the primary particles may also have undergone oxidation and hydroxylation.

In an attempt to further confirm the presence of layered Si-based planes in these samples, Si K-edge X-ray absorption fine structure (XAFS) analysis was performed. The X-ray absorption near edge structure (XANES) spectra for the two samples and for $CaSi_2$ are shown in Fig. 3(A), from which it is evident that the energy of the absorption edge of the siloxene samples is essentially equal to that of $CaSi_2$, since characteristic absorption peaks appear at 1841 and 1848 eV in each spectra. The peak at 1841 eV has been observed for both

$CaSi_2$ and c-Si,[22] suggesting a valence of Si^0 for the Si-Si bonds in the Si planes. The peak at 1848 eV, attributed to the presence of Si^{IV} and associated with Si-O bonding,[22] likely results from the surface oxidation that has been reported to occur in Kautsky siloxene structures.[16]

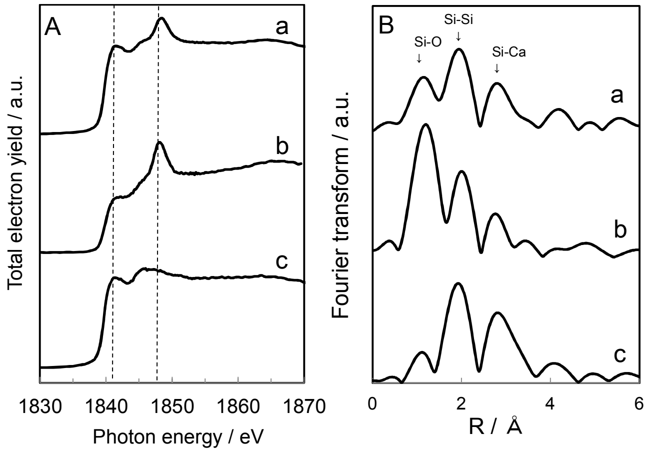


Fig. 3 Si-K edge XAFS data: (A) XANES spectra and (B) Fourier transforms of k^2-weighted EXAFS spectra of (a) CS0.25, (b) CS2.5, and (c) $CaSi_2$.

Fourier transforms of k^2-weighted extended X-ray absorption fine structure (EXAFS) spectra of the samples are shown in Fig. 3(B). Here peaks corresponding to Si-Si and Si-Ca bonds are observed for the Ca-siloxenes. A peak due to Si-O bonding is evident in the case of the CS2.5 sample due to the formation of Si-O-Si bonds in the Si planes within the siloxene structure induced by the higher Cl_2/Ca molar ratio. Ca is bound to Si through the remaining original Si-Ca bonding, judging from the presence of the peak derived from Si-Ca. The calculated average Si-Si bond length from fitting the Fourier transformed spectra was 2.400 Å for CS2.5, a value that is almost equal to that in $CaSi_2$ (Table S2). The average Si-Si bond lengths in 3D Si compounds such as c-Si and a-Si are known to be in the vicinity of 2.35 Å.[23] In the present study, however, the Si-Si bond length was almost the same as that of the original $CaSi_2$, while the Si-Ca bond length increased slightly from 3.090 nm in $CaSi_2$ to 3.128 nm in CS2.5, presumably due to the decreased interlayer Si-Ca bonding resulting from the Ca deintercalation. These results provide evidence for the preservation of 2D Si-based planes and the absence of a 3D Si network in the Ca-siloxene following the synthesis procedure.

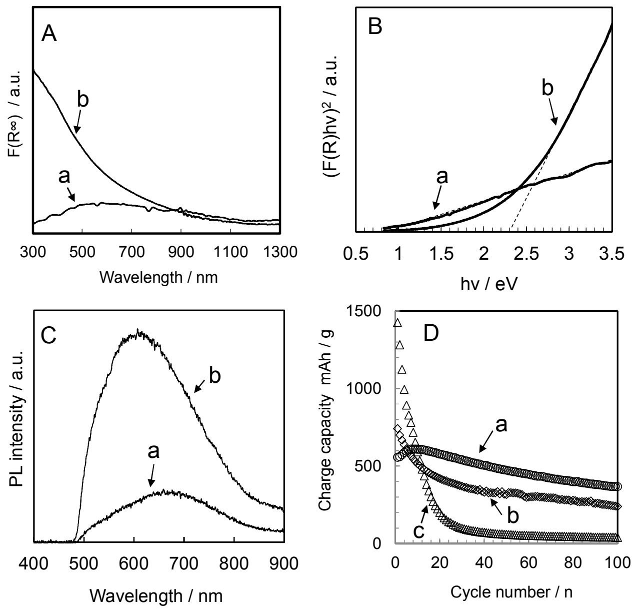


Fig. 4 Room temperature optical properties of Ca-siloxenes: (A) UV/Vis spectra, (B) tauc plots based on UV/Vis data, and (C) PL spectra of (a) CS0.25 and (b) CS2.5, and (D) charge capacity throughout 100 charge/discharge cycles: (a) CS2.5, (b) Kautsky-type siloxene, and (c) c-Si.

The Ca-siloxene samples exhibited an obvious absorption band spanning the visible and ultraviolet region in their UV/Vis absorption spectra at room temperature under air (Fig. 4(A)). Interestingly, the Ca-siloxene samples also demonstrated semiconducting characteristics with a direct band gap as a result of the Ca deintercalation (Fig. 4(B)), in contrast to the metallic character of $CaSi_2$. The optical band gap was found to vary from 1.0 eV in CS0.25 to 2.3 eV in CS2.5 and the electron conductivity of pelletized samples was also changed, from 6.4×10^{-4} S cm^{-1} in CS0.25 to 4.8×10^{-8} S cm^{-1} in CS2.5, again due to deintercalation. The room temperature, ambient atmosphere photoluminescence (PL) spectra of the Ca-siloxene samples using He-Cd laser (442 nm) and a cut off filter (< 495 nm) in front of the monochromator showed a broad luminescence band ranging from 500 to 800 nm (Fig. 4(C)). The emission peak for CS2.5 is at 600 nm (ca. 2.1 eV), a value that is almost equal to its bandgap energy. In contrast, CS0.25 has a weak emission peak at 675 nm (ca. 1.8 eV), a value that exceeds its bandgap energy, likely because the deep deintercalated regions acted as localized impurities. Therefore, it appears possible to tune the bandgap of Ca-siloxene by varying the extent of Ca deintercalation.

Ca-siloxene is characterized by Si-Ca-Si bridging between its interlayers, in contrast to a simple stacked siloxene structure in which only van der Waals interactions are present. One potential application for this unique structure is as a Li storage anode material in Li ion batteries. Compared to c-Si and Kautsky-type siloxene,[16] Ca-siloxene has been shown to maintain a large capacity following 100 charge/discharge cycles, due to the structural stability of its 2D siloxene layers brought about by Ca bridging (Fig. 4(D)). Thus, Ca-siloxene is expected to possess sufficient structural stability for future applications requiring durability, such as reversible electrode reactions, in addition to the normal chemical stability typical of silicon-based materials.

Conclusions

Ca-siloxene composed of Ca-bridged, fragmented Si planes was synthesized by a solid state reaction with ethanol wash involving the Ca deintercalation of $CaSi_2$ using $TaCl_5$. This Ca-siloxene exhibited tunable semiconducting properties based on varying the extent of deintercalation, including bandgap energy, conductivity and light emission, as well as structural stability as a Li storage material for Li ion batteries. These properties show promise for future applications to energy storage and conversion.

The authors thank to Ms. Akiko Ueki of Toyota central R&D Labs. for the assistance of TEM analysis. The XAFS experiments were conducted at the BL6N1 of Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan (Proposal No.201402013).

Notes and references

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Electronic Supplementary Information (ESI) available: Experimental detail, overview of siloxene structures, N_2 adsorption-desorption isotherm, composition, and fitting EXAFS data. See DOI: 10.1039/c000000x/

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