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# Novel Two-Dimensional Siloxene Material for Electrochemical Energy Storage and Sensor Applications

*Rajendran Ramachandran, Zong-Xiang Xu and Fei Wang*

## Abstract

After discovering graphene, the two-dimensional materials have gained considerable interest in the electrochemical applications, especially in energy conversion, storage, and bio-sensors. Siloxene, a novel two-dimensional low-buckled structure of Si networks with unique properties, has received the researcher's attention for a wide range of applications. Though the electronic and optical properties of siloxene have been explored in detail previously, there is a lack of electrochemistry studies of siloxene as the result of material degradation, and the investigation is still open-ended to enhance the electrochemical application. Recently, siloxene has been used for supercapacitor, lithium-ion batteries, and dopamine bio-marker detections. This chapter highlights the recent development of siloxene synthesis and its electrochemical properties in energy and sensor applications. The planar Si structure with Si<sub>6</sub> rings interconnected with different oxygen, hydroxyl functional groups, and large interlayer spacing of siloxene sheets can promote the active sites for enhanced electrochemical performance. This chapter provides the current state-of-the-art in the field and a perspective for future development in the electrochemistry field of siloxene.

**Keywords:** siloxene, electrochemistry, functional groups, active sites

## 1. Introduction

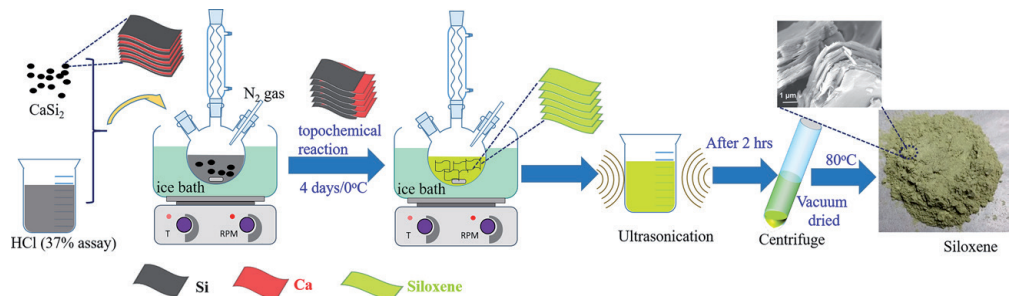
After discovering graphene in 2004, the two-dimensional (2D) materials have drawn significant attention in broad applications due to their unique physico-chemical properties. The 2D materials such as transition metal dichalcogenides (TMDs), phosphorene and bismuthine, etc., which consists of a one-atom-thick monolayer network can exhibit different chemical and physical properties, including the electrical and thermal conductivity, magnetic, photonic and catalytic properties when compared to their bulk counterparts [1]. Over the past few years, the enormous 2D family materials like graphene [2, 3], molybdenum disulphide (MoS<sub>2</sub>) [4, 5], tungsten disulphide (WS<sub>2</sub>) [6, 7], graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) [8] and recently MXene [9, 10] have been investigated for various applications in electronic, energy, catalysis and electrochemical applications. However, the electrochemistry investigation of those materials is yet to be explored in detail.

The limitation in the bandgap of these materials has hindered their performance in practical applications. Therefore, exploring a new novel 2D material is highly recommended, especially for the future electrochemical energy conversion, storage, and biosensors applications. Recently, silicon (Si) based one-atom-thick layered material named siloxene has been investigated for electrochemical energy and sensing applications, including supercapacitors, batteries, and dopamine sensors [1, 11–13].

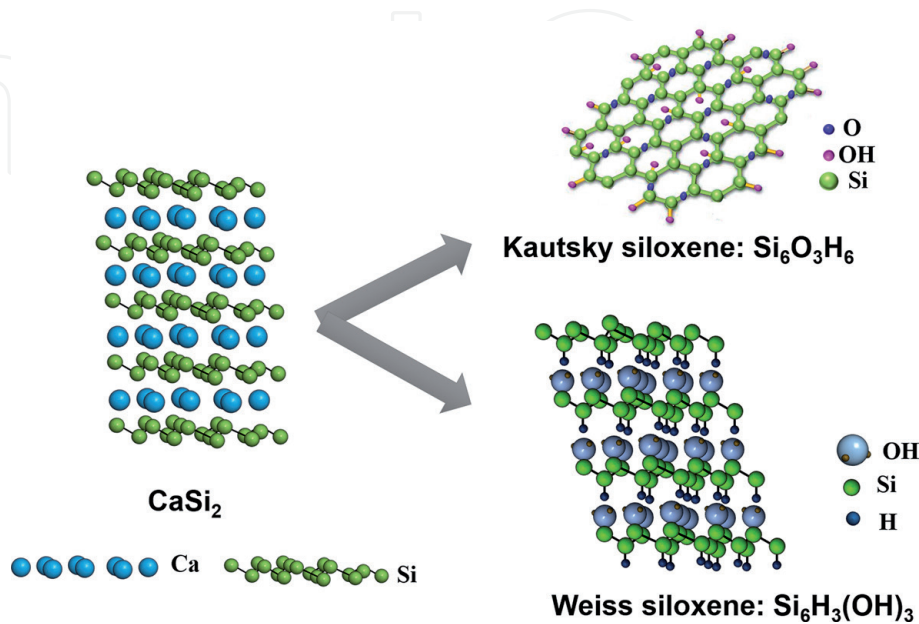
Siloxene is a direct bandgap material that was discovered by Wohler in 1863. It can be obtained through the deintercalation of calcium and exfoliation from the Zintl phase of calcium silicide ( $\text{CaSi}_2$ ) powder [14–16]. Different from the graphene planner structure, siloxene possesses a low-buckled structure due to its double band role. As a result of the surface-terminated functional groups with Si chain and the mixed  $\text{sp}^2$  and  $\text{sp}^3$  hybridization, siloxene can provide several advantages in the electrochemical energy and sensor applications [1, 11, 12, 17].

1.1 Synthesis of siloxene and its structural types

Siloxene is prepared by deintercalation of  $\text{Ca}^{2+}$  from  $\text{CaSi}_2$  under concentrated hydrochloric acid. Briefly, the required amount of  $\text{CaSi}_2$  powder and HCl acid stirred in the ice-cold condition under the inert gas atmosphere for 2-4 days (**Figure 1**). During this reaction, the deintercalation of Ca layers and functionalization of Si

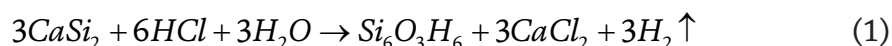


**Figure 1.** Siloxene synthesis process (reproduced from [11] with permission from Elsevier).



**Figure 2.** Different types of Siloxene structure [19].

sheets can be occurred simultaneously and formed the siloxene structure. The following equation can describe the common formation mechanism of siloxene from  $\text{CaSi}_2$  [11].



In general, the siloxene stoichiometric ratio of Si:H:O is 2:2:1. Based on the exfoliation and deintercalation conditions such as reaction time, the concentration of the acidic medium, and temperature, siloxene can be classified into two major types. (1) Weiss, and (2) Kautsky type siloxene structures [18]. In Weiss type siloxene ( $\text{Si}_6(\text{OH})_3\text{H}_3$ ), the six-membered  $\text{Si}_6$  rings connected with alternative Si-H and Si-OH bonds, whereas Kautsky type siloxene ( $\text{Si}_6\text{O}_3\text{H}_6$ ), the  $\text{Si}_6$  rings connected by Si-O-Si bridge (**Figure 2**). It is noteworthy that the crystalline silicon (common impurity) in  $\text{CaSi}_2$  may affect the siloxene structure formation [19], which deviates from the structures mentioned above.

## 2. Electrochemical application of siloxene

Due to the unique 2D structure and the abundant functional groups of siloxene, it can be applied in various applications such as optoelectronics, catalysis, water splitting, etc. Theoretical investigations of the siloxene have shown the high possibilities in different electrochemical applications [20]. However, because of limited knowledge of siloxene's electrochemistry, only a few works have been reported on the electrochemical application of siloxene so far. The siloxene has been mainly employed in supercapacitors and batteries as an electrode material and detection of biomarkers in electrochemical biosensors.

### 2.1 Supercapacitors

#### 2.1.1 Siloxene based supercapacitors

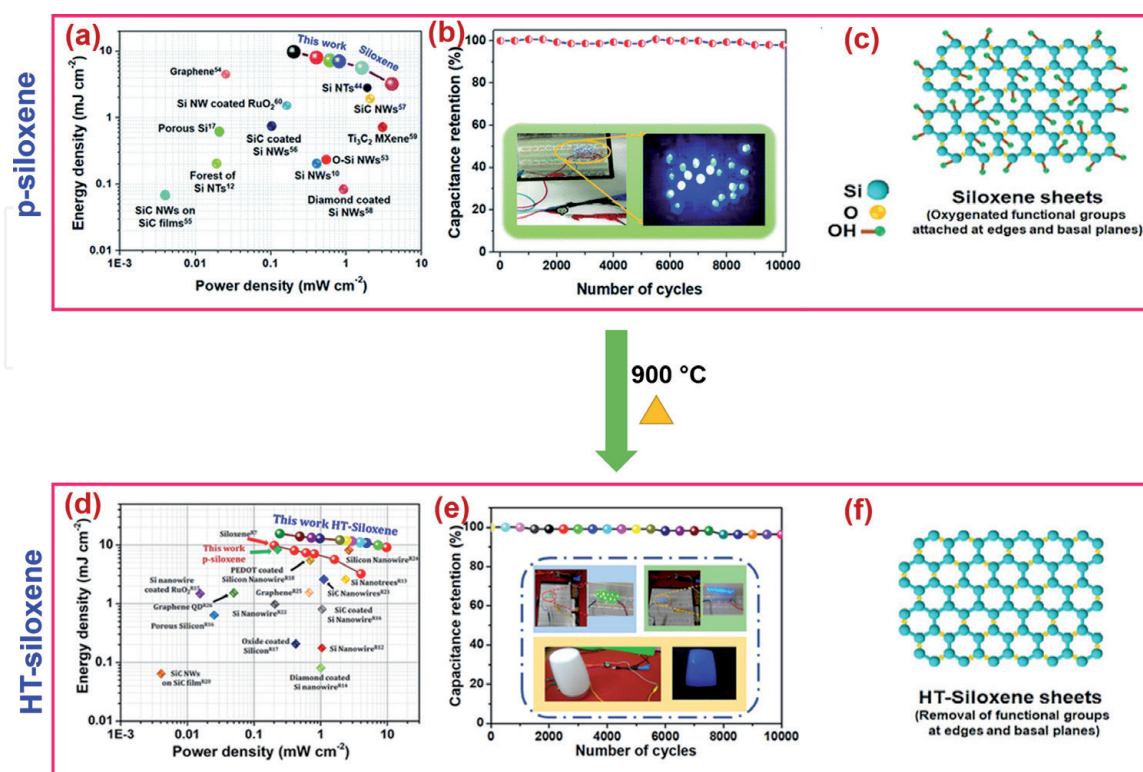
Though siloxene was discovered in 1863, it has recently received considerable attention in the electrochemical energy storage application. The researchers have been focused on siloxene based electrode materials for energy storage and conversion application. Due to the increases in energy consumption and the non-renewable sources decreasing gradually, the development of high-efficiency energy storage devices is highly demanded. Electrochemical or supercapacitors are the perfect choice for high-performance devices as the results of its high-power density and long cyclic lifetime [21]. Compared with the commercial activated carbon-based supercapacitors, the integration of Si-based materials with the current microelectronic technology can lead to higher performance in energy storage devices because of its high theoretical capacity ( $3579 \text{ mA hg}^{-1}$ ). However, Si-based materials such as silicon carbide ( $\text{SiC}$ ), Si nanowire, porous silicon have been employed as electrode materials in supercapacitor application, the functionalization of the one-atom-thick Si layers with interconnected  $\text{Si}_6$  rings can accommodate the better performance in supercapacitors [1].

Krishnamoorthy et al. have reported the siloxene based symmetric supercapacitor (SSC) application in 2018 [1]. The Kautsky-type of siloxene structure prepared by deintercalation of calcium from  $\text{CaSi}_2$  and confirmed its Si-O-Si bridges  $\text{Si}_6$  rings interconnection by Fourier transform infrared spectroscopy.



The capacitance behavior of the siloxene has been studied in tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) electrolyte under optimal conditions. Interestingly, the operating potential window (OPW) of the siloxene-SSC device was determined from 0 to 3.0 V. This result confirms the excellent electrochemical stability of the SSC device even at a higher voltage window. The fabricated SSC device showed unique capacitance behavior with an energy density of 5.08 W h kg<sup>-1</sup> (areal energy density of 9.82 mJ cm<sup>-2</sup>) and about 98% of capacitance retention even after 10 k cycles (**Figure 3**). The ion diffusion and the electron transfer rate were significantly enhanced by the conductive hexagonal Si frameworks in the siloxene during the electrochemical redox reactions. Also, the high surface area and the larger interlayer spacing between the siloxene sheets were enabled fast ion transport and improved the electrochemical performance of the SSC device.

It is well known that the reduced graphene oxide (rGO) can increase the electroactive sites for the electrochemical reactions than bare graphene oxide (GO) because of its higher electronic conductivity [22]. The electrical conductivity of siloxene sheets may decrease when a higher amount of the oxygen functional groups is attached on its edge/basal surface; thus, the reduction of oxygen functional groups in siloxene enhances the active sites for electrochemical redox reactions due to its better conductivity. In this scenario, Parthiban et al. have investigated the removal of oxygen functional groups in pristine siloxene (p-siloxene) at high temperatures and obtained reduced siloxene sheets (denoted as HT-siloxene). Calcinating siloxene sheets removed the functional groups at edge/basal planes of siloxene at 900°C, which led to the formation of reduced siloxene sheets [23]. Interestingly, the calcination process has decomposed the oxygen functional groups at edge/basal planes of siloxene and preserved the Si<sub>6</sub> rings' connection with oxygen atom without affecting the 2D layer structure. The obtained HT-siloxene possessed a higher electrical conductivity than p-siloxene resulting in improved



**Figure 3.** (a, b) Ragone plot and cyclic stability of p-siloxene SSC device; (c) structure of p-siloxene [1]; (d, e) Ragone plot and cyclic stability of HT-siloxene SSC device; (f) structure of HT-siloxene (reproduced from [23] with permission from ACS).

electrochemical performance. The specific capacitance of the HT-siloxene increased almost 1.71 times higher than that of p-siloxene. The maximum energy density of the HT-siloxene SSC device has been achieved by about  $6.64 \text{ Wh kg}^{-1}$ , higher than p-siloxene ( $3.89 \text{ Wh kg}^{-1}$ ) due to its lower equivalent series resistance and better electrical conductivity. The complete removal of the oxygen functional groups in p-siloxene enhanced the energy density of SSC. It also increased the cyclic stability of the SSC (96.3% after 10000 cycles), as shown in **Figure 3**.

Another fascinating strategy has been developed by Kim and co-workers recently that dry reforming methane (DRM) recycled siloxene/Ni foam catalyst towards supercapacitor applications. The siloxene coated Ni foam was initially utilized for DRM reactions for producing  $\text{H}_2$  and CO gas by  $\text{CO}_2$  reduction. After the DRM reaction, the siloxene/Ni foam catalyst has employed as electrode material in SSC [24]. The regeneration of carbon during the DRM reactions deposited on the siloxene/Ni foam catalyst and could improve the electrochemical performance. Compared to the p-siloxene and HT-siloxene, the carbon-coated siloxene/Ni foam exhibited superior performance in the supercapacitor. A maximum energy density of  $30.81 \text{ Wh kg}^{-1}$  was achieved for carbon/siloxene/Ni foam-based SSC, indicates the remarkable performance enhancement. Thus, utilizing spent siloxene catalysts to supercapacitor can be an effective approach for waste-to-energy applications. Besides, the direct use of the siloxene in a supercapacitor, siloxene was also confirmed as a flexible template for fabricating silicon oxy-carbide (SiOC). Carbothermal conversion of siloxene to SiOC has been proposed by Pazhamali and co-works [12]. Mixing siloxene and sodium alginate at  $900^\circ\text{C}$  led to the formation of SiOC. Since the SiC-based electrodes can intensify the cycling stability and areal capacitance in supercapacitors, the SiOC electrodes were expected to improve the stability of the SSC device than siloxene based SSC. The SiOC based SSC device delivered an excellent electrochemical performance with an energy density of  $20.89 \text{ Wh kg}^{-1}$ , which is higher than that of p-siloxene. However, the cyclic stability of SiOC supercapacitor decreased to 92.8% after 5000 cycles. As pointed out in the previous paragraph, the removal of oxygen functional groups can improve the SSC performance; the complete reduction of oxygen in SiOC may help to facilitate the fast ion transport and wettability of the electrode during the long cyclic time.

#### 2.1.2 Siloxene composite supercapacitor

Making composite electrodes is an efficient approach to increase the supercapacitor's electrochemical performance due to its synergistic behavior [25]. The specific capacitance of siloxene is restricted because of its aggregation effect; consequently, the layers agglomerations generate poor utilization of the pores and the lower specific surface area. Thus, introducing a spacer material such as metal oxides or carbon between the siloxene sheets can enhance the accessible sites for the electrochemical reactions. Meng and co-works have reported the construction of a three-dimensional (3D) architecture of siloxene-reduced graphene oxide hydrogel (SGH) through a simple hydrothermal method (**Figure 4**) [26].

The hybrid structure of SGH has increased the specific surface area and facilitated the electrolyte ions transportation, resulting in improved capacitive performance. As compared to bare siloxene electrode specific capacitance ( $23 \text{ F g}^{-1}$ ), the SGH with 1:3 ratio composite electrode exhibited a maximum specific capacitance of  $520 \text{ F g}^{-1}$  at a current density of  $1 \text{ A g}^{-1}$ . However, the EDLC of the graphene in SGH has contributed significantly to the capacitive enhancement of siloxene-graphene composite. Though graphene could facilitate the capacitance performance, the surface oxygen-functional groups of siloxene provided pseudocapacitance and improved the wettability of the electrode, results in an excellent rate capability and outstanding cyclic stability.



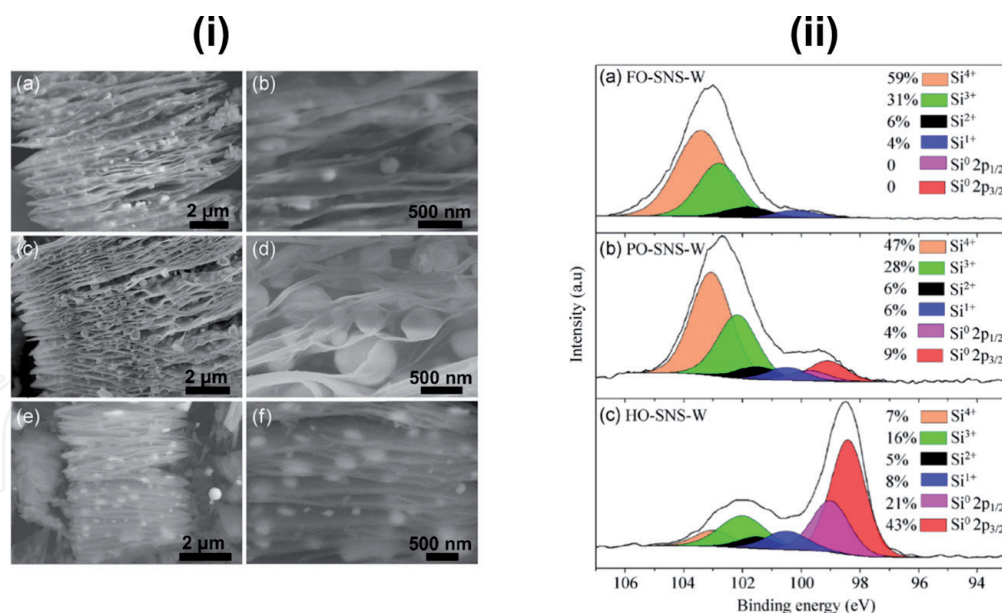
**Figure 4.** Synthesis of siloxene-reduced graphene oxide hydrogel and its specific capacitance plot [26].

## 2.2 Siloxene application in batteries

Like supercapacitors, rechargeable batteries (e.g., lithium-ion batteries, sodium-ion batteries, lead-acid, etc.) are primary power sources for large-scale portable and wearable electronic devices. They have received significant consideration due to their high energy density and long cyclic stability [27, 28]. However, the current battery technologies cannot meet the advanced application requirement as the result of confined energy storage capacity. Thus, the development of commercial electrodes in the existing technologies is highly needed.

The theoretical capacity of silicon (Si) is  $4200 \text{ mA hg}^{-1}$  [29], which is higher than the capacity of graphite ( $372 \text{ mA hg}^{-1}$ ), has considered being an active anode material for the future lithium-ion batteries (LIBs). However, the severe capacity degradation and the high-volume change during the lithiation-delithiation process may lead to lower Coulombic efficiency. Making 2D Si nanosheets with oxygen functional groups provides a high specific surface area, resulting in fast lithium storage and preventing volume changes. As mentioned in the previous section, the siloxene oxidation level can be controlled by the various synthesis conditions such as temperature, oxidants, concentrations, etc. The oxidation level may influence the lithiation-delithiation process. Xu and co-workers have demonstrated the siloxene preparation with different oxidation levels in the various oxidants and the temperature [30]. Three types of siloxene oxidation level have been achieved by altering the oxidants and temperature: (i)  $\text{CuCl}_2$  aqueous solution used to prepare fully oxidized siloxene nanosheet (FO-SNS) at room temperature; (ii) partially oxidized siloxene nanosheet (PO-SNS) made in  $\text{SnCl}_2$  ethanol solution at  $60^\circ\text{C}$  and (iii) hardly oxidized siloxene nanosheet (HO-SNS) synthesized in a  $\text{LiCl-KCl}$  molten salt at  $400^\circ\text{C}$  (**Figure 5(i)**). The FO-SNS, PO-SNS, and HO-SNS electrodes delivered the lithiation capacity of 298, 1218, and  $1450 \text{ mA hg}^{-1}$ . Besides, the HO-SNS presented a higher Coulombic efficiency of 66%, which is higher than FO-SNS (24%) and PO-SNS (56%). The improved performance of HO-SNS has associated with the presence of a higher atomic percentage (64%) of bulk Si ( $\text{Si}^0$ ) and the lower percentage (7%) of  $\text{SiO}_2$  ( $\text{Si}^{4+}$ ) in HO-SNS, which were estimated from the XPS analysis (**Figure 5(ii)**). Besides, the hierarchical nanostructure of HO-SNS could buffer the volume expansion and contribute to the good rate performance. Fu and co-workers have remarked that bare siloxene is an unsuitable anode material for LIBs due to its inadequate electrochemical capacity, resulting in the lower Coulombic efficiency. However, Si- derivatives such as silicon suboxides ( $\text{SiO}_x$ ), carbon-coated  $\text{SiO}_2$ , etc., from siloxene can meet higher capacity requirements with satisfactory Coulombic efficiency. Fu et al., have demonstrated the carbon-coated 2D  $\text{SiO}_x$  nanocomposites (nano-Si/ $\alpha$ - $\text{SiO}_2$ ) from siloxene to moderate the volume expansion during the electrochemical lithiation-delithiation process [31]. The carbon-coated nano-Si/ $\alpha$ - $\text{SiO}_2$  anode materials showed the limited volume change, fast electrons





**Figure 5.** (i) SEM images of (a, b) FO-SNS, (c, d) PO-SNS, (e, f) HO-SNS; (ii) XPS spectrum of siloxene samples at different oxidation (reproduced from [30] with permission from Springer).

transport, and more significant Li-ion kinetics, resulting in high initial Coulombic efficiency (72.5%) with a capacity of 946 mA hg<sup>-1</sup>. On the other hand, the value of x in SiO<sub>x</sub> can influence Li storage's electrochemical performance. Thus, controlling the oxidation level of the SiO<sub>x</sub> is a crucial process to achieve higher capacity than bare Si structures. Many previous studies showed that SiO<sub>x</sub> with x = 1.0 presented the specific capacity value higher than 1000 mA hg<sup>-1</sup> [32]. However, unsatisfactory cyclic life has limited its practical usage. Thus, turning the oxygen content in SiO<sub>x</sub> is a proper way to improve the electrochemical performance in LIBs. After investigating carbon-coated nano-Si/α-SiO<sub>2</sub>, Fu and co-workers have prepared siloxene with different levels of oxidation in SiO<sub>x</sub> and used as anode material for LIB. They controlled the SiO<sub>x</sub> oxidation level in the siloxene via stepwise oxidizing of the siloxene precursor at various times [32]. SiO<sub>x</sub> with four different oxidation levels, such as SiO<sub>1.01</sub>, SiO<sub>1.25</sub>, SiO<sub>1.47</sub>, and SiO<sub>1.78</sub> has been tailored through siloxene oxidation and investigated their Li-storage capacity. The sample SiO<sub>1.47</sub> exhibited optimal electrochemical behavior due to the synergistic effect of electrical conductivity and Li-ion diffusivity. The higher oxygen level in SiO<sub>x</sub> caused a larger polarization effect, resulting in the poor Coulombic efficiency and smaller reversible capacity.

Similar to the graphene-siloxene composite electrode in supercapacitors, the incorporation of siloxene sheets between the graphene layers enhances the specific surface area, facilitating the fast Li-storage. In the siloxene-graphene (SiG) composite, the siloxene sheets have provided higher Li-storage, and the encapsulated graphene sheets prevented the volume expansion during lithium insertion-extraction process. SiG anode material exhibited the initial cycle charge and discharge capacities of 3016 mA hg<sup>-1</sup> and 3880 mA hg<sup>-1</sup> with a capacity decay of 78%, which were higher than the bare siloxene and graphene electrodes. The synergistic effect of graphene and siloxene and the excellent electrical conductivity of graphene in the composite contributed to the higher electrochemical performance for LIBs [29].

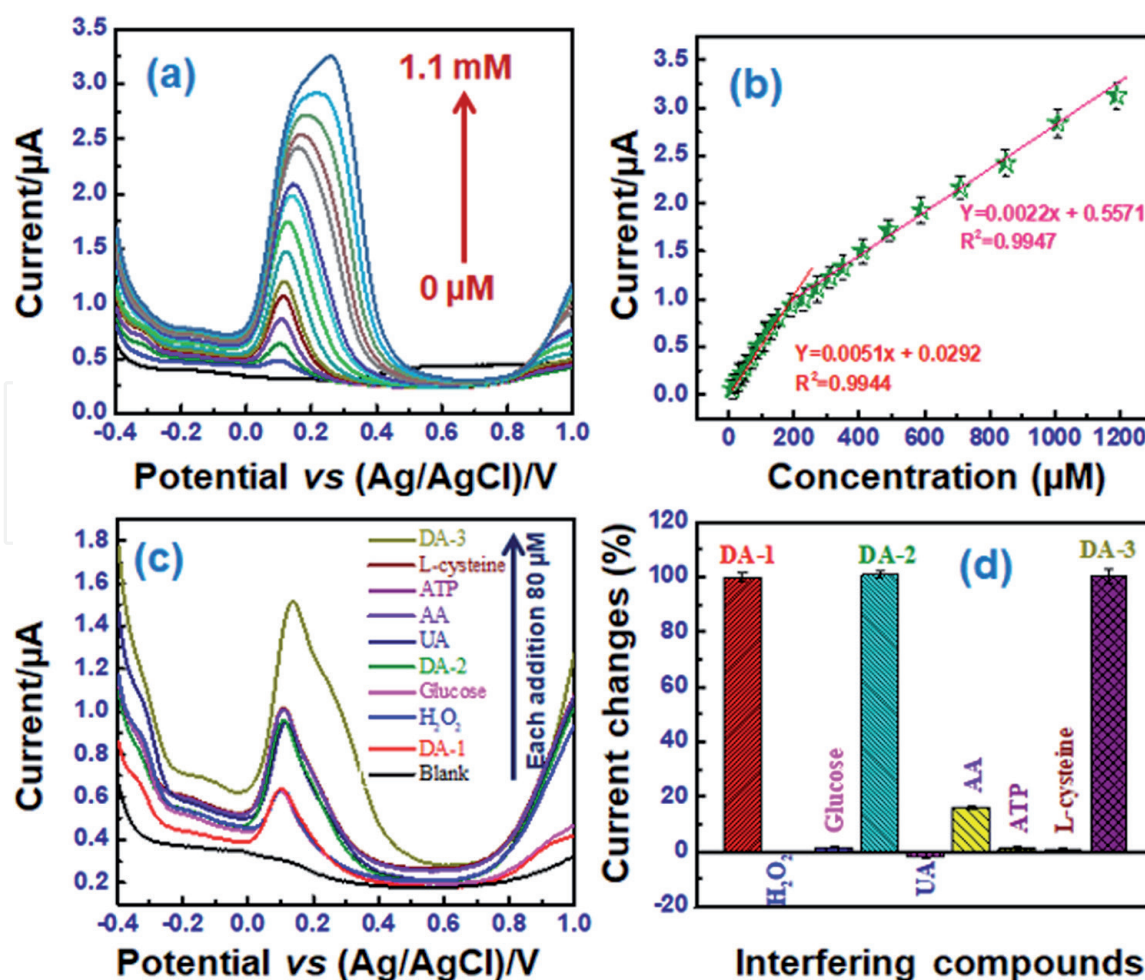
### 2.3 Siloxene based electrochemical sensor

The 2D siloxene sheets not only possessed the excellent electrochemical characteristics towards electrochemical energy application. Besides, due to the large



surface area and the unique 2D structure of siloxene, the heterogeneous electron transfer (HET) is high, which is beneficial for selective electrochemical bio-marker detections. We have recently demonstrated the siloxene-based novel electrochemical dopamine sensor and obtained remarkable achievements in dopamine detection by the siloxene modified sensor [11]. Dopamine (DA) is an important neurotransmitter that plays a crucial role in the central nervous system and cardiovascular systems. A variety of materials have been employed for electrochemical DA detection in the past decades. However, the high selectivity of DA is limited to the existing materials. As a result of high HET rates, large surface area, and improved mass transportation, siloxene possessed high selectivity for DA detection (**Figure 6**). Siloxene modified glassy carbon electrode showed a well-defined redox peak in the cyclic voltammetry technique towards DA detection. Excellent linearity has been achieved for the siloxene electrode in the presence of a different concentration of DA, and the modified electrode exhibited a detection limit of  $0.327 \mu\text{M}$ . Besides, the proposed sensor revealed a wide linear range from 10 to  $1100 \mu\text{M}$  (**Figure 6(b)**).

The DA detection performance by the 2D siloxene sheets is remarkably higher than that of other reported 2D graphene and  $\text{g-C}_3\text{N}_4$  modified electrodes. Siloxene sheets owned a higher response for the detection limit and showed high selectivity for DA detection. The stronger  $\pi$ - $\pi$  interaction between the siloxene planar structure and the dopamine phenyl structure enables faster electron transportation during the DA oxidation process, making the high selectivity characteristic of the siloxene modified electrode. On the other hand, the  $\pi$ - $\pi$  interaction of the siloxene structure with other biomolecules such as ascorbic acid, uric acid, etc., is weak, resulting in



**Figure 6.** (a-d) Electrochemical differential pulsed voltammetry response and linear range of siloxene modified electrode for DA detections (reproduced from [11] with permission from Elsevier).

the inactive oxidation. However, the thickness of the siloxene sheets can affect the electron conduction during the electrochemical reactions similar to graphene [33]. Reducing the size and the layer thickness of siloxene could tremendously enhance its performance for DA detection.

### **3. Summary and future research direction**

In conclusion, this chapter deals with the comprehensive review of the raising star 2D siloxene based electrochemical energy and sensor applications. The siloxene synthesis process and the siloxene structure affecting parameters have been reviewed in detail. The functional groups in siloxene and the oxidation level can be varied at different synthesis times and the annealing temperature. Compared to pristine siloxene, high temperature treated siloxene possessed an excellent performance in the electrochemical supercapacitors because of its reduced functional groups. Besides, the siloxene and its composite have been used as anode materials for LIBs and showed a significant capacity and Coulombic efficiency. Li-storage has influenced by the oxidation level in siloxene due to the presence of different atomic percentages of Si functional groups. However, both supercapacitors and LIBs applications, siloxene derivatives such as SiOx, SiOC showed improved performance as the results of its better electrical conductivity and Li-ion diffusivity compared to the bare siloxene. The reported siloxene works have focused on the performance of siloxene in supercapacitors and LIBs. But many works failed to investigate the insight of the electrochemistry of siloxene and its derivatives for better energy density, capacity, and cyclic stability. Thus, the research direction should be focused more on the study of electrochemistry of siloxene. On the other hand, the 2D siloxene sheets proved as a novel electrochemical sensor for highly selective dopamine detection. Moreover, the size and thickness of the layer can influence the HET rate, specific surface area, and active sites for DA detection, which need to be optimized in the near future.

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