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Silicene Quantum Dots Confined in Few-Layer Siloxene Nanosheets for Blue Light-Emitting Diodes

Xinling Xu, Liping Zhou, Degong Ding, Yang Wang, Jingyun Huang,* Haiping He, and Zhizhen Ye*

School of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

KEYWORDS

silicene quantum dot; siloxene; photoluminescence; quasi-direct band gap; topochemical reaction

ABSTRACT

Two-dimensional silicon-based materials have unique physical and chemical properties due to high surface area and quantum confinement effects. Herein, a topochemical reaction method is used for preparing silicene quantum dots confined in few layer siloxene nanosheets with FeCl₃•6H₂O as oxidant, which shows thickness less than 2 nm. The experimentally prepared siloxene nanosheets are dispersible, with silicene quantum dots having average diameter less than 5 nm. The silicene quantum dots are self-organized through the oxidation of FeCl₃, showing unique optical properties of blue emission. The UV-visible absorption and PL emission spectra indicate the quasi-direct band gap transition to the emission. Besides, the few-layer siloxene nanosheets with silicene quantum dots have a radiative lifetime of 1.098 ns at an emission wavelength of 435 nm, which derives from the quasi-direct band transition of silicene quantum dots. Such twodimensional nanosheets of silicon possess potential applications for the emitting layer materials of blue light-emitting diodes (LED).

1. Introduction

Silicene is one type of silicon allotropes with unique low-buckled two-dimensional nanostructure, the oxide of which is siloxene, and both have special physical and chemical properties due to high surface area and quantum confinement effects.¹⁻⁴ Similar to graphene, silicene also has hexagonal honeycomb structure, and since Si and C belong to the same group in the periodical table, they display similar electronic properties.⁵⁻⁷ However, unlike graphene which consist of sp²-hybridized carbon atoms, Si atoms in the silicene prefer the interplay between sp³ and sp^2 hybrid bonds, resulting in a buckled hexagonal shape and a highly chemically active surface.^{5, 8} Compare to silicon quantum dots, the crystal structure of the silicene quantum dots is different, which is low-buckled 2D nanostructure formed by interconnected Si₆ rings instead of cubic crystal structure. Silicene quantum dot is a type of quasi-zero-dimensional material, in which the movement of the electrons in all directions is limited, resulting in more significant quantum confinement effects than silicon quantum dots. The properties of silicene make it possible to control the band gap and realize the surface functionalization to deliberately manipulate the physical, chemical, and electronic properties of silicene.⁹⁻¹¹ Therefore, the research on silicene and its oxides has received extensive attention. It is worth noting that silicene quantum dots of which the structural analogue is graphene quantum dots, have great future prospects for multiple application, such as bioimaging, chemical sensors, catalysis, energy storage, optoelectronics, and microelectronics, etc.¹²⁻¹⁵ Thus, it will be of fundamental and technological significance to examine the preparation methods, properties and potential applications of silicene quantum dots.

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The siloxene is one kind of oxidized two-dimensional silicon, having oxidized functional groups on the surfaces. Siloxene has different structures, and can be mainly classified into three types: (a) Weiss siloxene, (b) Chain-like siloxene, (c) Kautsky siloxene.^{16,17} Siloxene has also reported being a promising material in the fields of energy storage, electrochemistry, catalysis, sensors, optoelectronics and supercapacitors.¹⁸⁻²¹

At present, various methods available for the preparation of silicene and siloxene nanosheets are reported, such as epitaxy, chemical and electrochemical methods. Epitaxy is a bottom-up preparation method, which mainly includes the following: (a) molecular beam epitaxy (substrate materials including Ag(111), Ir(111), MoS₂, ZrC, ruthenium and graphite, etc);²²⁻²⁶ (b) epitaxial silicene by surface segregation from the substrate (the underlying substrate such as a (111)terminated silicon substrate under a ZrB₂ film providing silicon atoms);⁸ (c) intercalated silicene by intercalation through a silicide network (the ad hoc tailored silicidation including SrSi₂, EuSi₂, GdSi₂, where silicene nanosheets are incorporated as network constituents).⁸ Epitaxy methods can obtain silicene with integrity crystal and uniform thickness, but it is difficult to separate the silicene from the substrate. The operation of epitaxy is complicated, and the cost is high, which is not conducive to large-scale production. Chemical and electrochemical methods have the advantage of lower cost and can be prepared on a large scale, however, the thickness of products is uneven and the silicene nanosheets are easily oxidized. The principles of chemical and electrochemical methods that have been reported are mainly: (a) topotactic transformation of layered calcium silicide in the presence of hydrochloric acid (or a solution of propylamine hydrochloride) resulting in the formation of siloxene nanosheets; 17, 27-29 (b) magnesium thermal reduction of SiO₂ nanosheets at high temperature;³⁰⁻³³ (c) oxidant-mediated liquid oxidation and exfoliation of CaSi₂ resulting in the formation of silicene nanosheets (the oxidizing agent including I₂, CuCl₂ and SnCl₂,

etc);^{1,20} (d) one-step simultaneous molten salt-induced exfoliation and chemical reduction process for preparing high quality Si nanosheets;^{34,35} (e) chemical vapor deposition (CVD);^{36,37} (f) electrochemical lithiation and de-lithiation of silicon resulting in the formation of few-layer silicene nanosheets and their oxides;^{38,39} (g) DC arc discharge method to synthesize twodimensional ultrathin silicon nanosheets.⁴⁰

While silicene and siloxene nanostructures have been extensively studied in the fields of lithium ion batteries and supercapacitors, optical properties of silicene quantum dots and siloxene nanosheets are rarely reported.^{5, 41-42} In this work, silicene quantum dots confined in few-layer siloxene nanosheets are synthesized by a topochemical reaction, which chooses FeCl₃•6H₂O as oxidant. The experimentally prepared siloxene nanosheets are dispersible, the thickness of which is generally less than 2 nm, and the calculation shows that the number of two-dimensional Si plane layers is within five. Silicene quantum dots are self-organized in siloxene nanosheets show unique optical properties of blue emission, and time-resolved PL measurement showed a radiative lifetime of 1.098 ns at an emission wavelength of 435 nm, which derived from the quasi-direct band transition of silicene quantum dots. This work demonstrates an original method for preparing silicene quantum dots confined in few-layer siloxene nanosheets, showing potential applications in the field of blue LED light-emitting layers due to the strong blue emission.^{2, 8, 43}

2. Results and Discussion

Figure 1 shows the atomic structure of $CaSi_2$ and the schematic representation of the formation mechanism of siloxene nanosheets under three different conditions (prepared via topochemical reaction of layered $CaSi_2$). The layered structure of $CaSi_2$ is formed by interconnected Si_6 rings forming 2D corrugated Si planes and Ca^{2+} planar monolayers spacer stacking, as shown in Figure

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1a.²⁰ CaSi₂ is a strong reductant due to the highly electronegative Si^{-,1} In a suitable reaction medium, when reacted with oxidants, such as HCl or FeCl₃, Ca ions are deintercalated from CaSi₂ and formed into siloxene nanosheets containing various functional groups (Figure 1b-e). As a result of the unique structure of CaSi₂, the siloxene nanosheets maintain their structural integrity after topochemical reactions. The structures of the siloxene nanosheets and the functional groups on which are different depending on the distinct reaction solvent and oxidant. Upon the topochemical reaction in hydrochloric acid at room temperature, it forms Si₆ rings interconnected with oxygen, i.e. siloxene nanosheets, which contain functional groups such as Si-OH, Si-H and OSi₂=Si-H on the edges and surfaces of the nanosheets (Figure 1c, HCl-Siloxene). When CaSi₂ is pre-decalcified in ethyl acetate and then reacted with hydrochloric acid, amorphous silicon-rich aggregated regions are formed in the siloxane nanosheets, the edges and surfaces of which contain few functional groups (Figure 1d, EAC-Siloxene). Under the oxidation of FeCl₃, CaSi₂ is decalcified in ethyl acetate, and after removing the impurities in the products by hydrochloric acid reaction, silicene quantum dots are self-organized in the siloxene nanosheets, with few functional groups at the edges and surfaces of the nanosheets (Figure 1e, QD-Siloxene). All the three types of siloxene nanosheets show optical properties of blue emission under the excitation of ultraviolet light, but the luminescence peak positions, radiative lifetimes and luminescence mechanisms of which are different. To the best of our knowledge, $FeCl_3$ is used as oxidant in the topochemical reaction for the first time, which has never been used to react with CaSi2 to prepare siloxene nanosheets in ethyl acetate. When CaSi₂ is decalcified by ethyl acetate, since the ultra-thin Si nanosheets have a large number of defects and extremely high surface energy, it is easy to form siloxene and silicon-rich regions at the defects due to the oxygen functional groups and free Si in the solvent, which belongs to a self-organization process. In the absence of $FeCl_3 \cdot 6H_2O$, the

silicon-rich regions contain a large amount of bridging oxygen atoms, which shows an amorphous state. However, under the strong oxidation of FeCl₃, the oxygen atoms will leave the nanosheets, and the ability of agglomeration between the nanosheets will be weakened. Si can spontaneously assemble at the defects of nanosheets, presenting a crystalline state, and the agglomeration of the nanosheets can be reduced by FeCl₃, forming the silicene quantum dots confined in few-layer siloxene nanosheets.



Figure 1. Schematic illustration for the preparation of silicene quantum dots confined in few-layer siloxene nanosheets. a-b) Preparation of siloxene nanosheets from CaSi₂ via a topochemical reaction. c) Structure of the HCl-Siloxene prepared in hydrochloric acid. d) Structure of the EAC-Siloxene prepared in ethyl acetate. e) Structure of the QD-Siloxene prepared in ethyl acetate with FeCl₃.

The X-ray diffraction (XRD) patterns of the samples are shown in Figure 2a. The HCl-Siloxene and EAC-Siloxene nanopowders can be indexed to PDF#27-1402, which show the typical crystalline silicon structure based on the (111) peak at 28.5°, and the samples also contain amorphous silicon oxide due to the broad hump at $15^{\circ} \sim 25^{\circ}$. It indicates that the 2D Si planes is liable to be stacked and formed into thick silicon crystal via the topochemical reaction without FeCl₃. Therefore, the yield of siloxene nanosheets is small, and the XRD patterns exhibit strong crystal peaks. In addition, since the structure of CaSi₂ is crystal, the Si atoms are arranged in longrange order. During the process of decalcification, some Si atoms are still ordered. The 2D corrugated Si planes have high surface energy, and there are a large number of oxygen functional groups in the solvent. Therefore, in addition to agglomeration to form silicon nanocrystals, there are also some ordered Si planes which agglomerate and combine with bridging oxygen atoms. After drying in vacuum at 60 °C, polysilicon oxides (SiO_x) are formed, showing weak peaks in the XRD profiles. The addition of FeCl₃ as an oxidant can promote the delamination of bulk $CaSi_{2}$, which increases the yield of ultra-thin siloxene nanosheets. For the QD-Siloxene samples prepared by $FeCl_3$ as oxidant, the peaks of siloxene nanosheets are indexed to the tetragonal phase of PDF#39-0973 and the allo-Si metastable phase of PDF#41-1111, as shown in Figure 2a and Figure S6. Besides, the crystal peak intensity of QD-Siloxene is significantly weakened, indicating that the two-dimensional Si planes formed by the topochemical reaction are not easy to stack, but most of which are oxidized to form ultra-thin nanosheets. The appearance of the allo-Si metastable phase (PDF#41-1111) indicates that the samples contain crystalline silicene, and the peak of the tetragonal phase (PDF#39-0973) is produced by thicker crystalline silicene planes. This finding is very consistent with previous studies of 2D silicon nanosheets prepared by lithiation and delithiation processes.³⁸



Figure 2. a) X-ray diffraction patterns, b) Laser Raman spectra, c) Fourier Transform Infrared spectrum of the products, and X-ray photoelectron spectra for Si 2p states of d) HCl-Siloxene, e) EAC-Siloxene, and f) QD-Siloxene.

The crystallinity and bonding nature of the three kinds of siloxene nanosheets are examined by laser Raman spectroscopy as shown in Figure 2b and Figure S8. The Raman spectra of the HCl-Siloxene nanosheets shows two sharp bands at 488 and 513 cm⁻¹, which confirms the presence of Si–O/Si–OH and Si–Si groups, respectively, and the broad peak at 732 cm⁻¹ is consistent with the presence of Si-H bonds.²¹ The vibrational peaks of Si-O/Si-OH and Si-H disappear in the Raman spectrums of EAC-Siloxene and QD-Siloxene nanosheets, which confirms that the Si-OH, Si-H bonds of siloxene nanosheets are reduced in ethyl acetate. The weak band observed at 380 cm⁻¹ for all the samples is attributed to the vibration of Si-Si bond.¹⁶ For the HCl-Siloxene and EAC-Siloxene nanosheets, the sharp band at 513 cm⁻¹ corresponds to the vibration raised from symmetric stretching (E_{2g}) modes of the Si–Si bonds, while the corresponding peak of the bulk

crystalline silicon is at 520 cm^{-1.17} It is reported that the full width at half-maximum (FWHM) of the Si-Si peak is widened and moves to the low frequency as the thickness of the nanosheets decreases.⁴⁴ The vibrational peak of Si-Si (E_{2g}) in the QD-Siloxene is at 508 cm⁻¹, indicating that the thickness of the QD-Siloxene nanosheets is lower than those of HCl-Siloxene and EAC-Siloxene nanosheets, which confirms that FeCl₃ contributes to the layered stripping of CaSi₂, and the two-dimensional structure of the corrugated Si planes is maintained after topochemical reaction process.

The bonding nature of the functional groups present in the HCl-Siloxene, EAC-Siloxene and QD-Siloxene nanosheets are examined using Fourier Transform Infrared (FT-IR) spectroscopy, as shown in Figure 2c. The FT-IR spectrum of the HCl-Siloxene nanosheets shows the presence of broad vibration bands at 460, 876, 1077, 1643 and 2114 cm⁻¹, which correspond to the vibrations raised from the v(Si-Si), v(Si-H), v(Si-O-Si), v(Si-OH) and v(OSi₂=Si-H),²¹ which indicates that the siloxene nanosheets have a Kautsky structure. It is reported that the Kautsky structure in 2D Si planes is mainly composed of Si₆ rings interconnected through Si-O-Si bridges.¹⁶ For EAC-Siloxene and QD-Siloxene nanosheets, the bands observed at 460, 876, 1073 cm⁻¹ correspond to the vibrational strengths of v(Si-OH) and v(OSi₂=Si-H), v(Si-O-Si), v(Si-O-Si), respectively. It shows that the vibrational strengths of v(Si-OH) and v(OSi₂=Si-H) are obviously weakened, indicating that the functional groups of siloxene nanosheets are effectively reduced via the ethyl acetate used as the pre-decalcification medium, comparing with hydrochloric acid. The broad band observed at 3400 cm⁻¹ corresponds to the hydroxyl groups on the surfaces of the siloxene nanosheets.¹⁷

The chemical composition and valence state of Si in HCl-Siloxene, EAC-Siloxene and QD-Siloxene nanosheets are determined by XPS measurements (Figure 2d-f). It can be clearly found that five different peaks centered at about 26, 103, 154, 285 and 533 eV in the full scan (Figure

S1a-c, Supporting Information), which correspond to O 2s, Si 2p, Si 2s, C 1s, and O 1s states, respectively.⁴⁵ In order to understand the oxidation states of Si more clearly, the peak-fitting of the Si 2p peak is performed, and Figure 2d-f show the XPS binding energy of Si 2p peak of HCl-Siloxene, EAC-Siloxene and QD-Siloxene. From the binding energies, the peak at about 99.5 eV is attributed to bulk Si (Si⁰).⁵ The three other peaks between 100 and 103 eV are related to specific binding energies for Si^{1+} , Si^{2+} , and Si^{3+} oxidation states, respectively, while the peak at 103.5 eV belongs to SiO₂ (Si⁴⁺).^{5, 20} In the high-resolution scan in Figure 2f, the peaks falling in the intermediate between 99.5 eV and 103.5 eV contain peaks belonging to the few-layer silicene quantum dots. In addition, the high-resolution scan of Fe 2p in the QD-Siloxene (Figure S1d, Supporting Information) shows that there is only a trace amount of Fe residual (less than 1%) in the products. The peak of Fe 2p is difficult to use software to separate, which indicates that there are few metal impurities remaining in the QD-Siloxene nanosheets. From the high-resolution scans of the three kinds of samples, it is found that the main oxidation state of Si is Si^{4+} (103.5 eV), which is caused by the topochemical reaction in liquid. The high-resolution spectrums also contain weak peaks of Si⁰, which is mainly due to the formation of thick Si crystals via the two-dimensional Si planes stacking during the reaction.

Dispersible siloxene nanosheets are obtained by ultrasonic exfoliation and centrifugation treatment. Figure 3a-b show typical scanning electron microscopy (SEM) images of QD-Siloxene nanosheets. The products after the topochemical reaction appears to be very different from the starting material, CaSi₂ (Figure S2a). The CaSi₂ is a deep gray polycrystalline powder with an inconspicuous layered structure, which gradually delaminates into layered stacking structure under the action of the specific solvents and oxidants. It is found that the pristine bulk CaSi₂ is transformed to exfoliated CaSi₂ with the loose stacking structure after reaction, ultimately

obtaining the adequately exfoliated siloxene nanosheets. It can be seen that cleavage occurs in many layers throughout the $CaSi_2$ particles, rather than via a layer-by-layer basis starting from the surface.



Figure 3. a-b) SEM, c) AFM, d) scanning transmission electron microscopy (STEM), and e) HRTEM images of QD-Siloxene nanosheets. f) The core-size histogram for the statistical analysis of silicene quantum dots.

The atomic force microscope (AFM) measurement shows the precise thickness of the QD-Siloxene nanosheets, which are dropped on a mica substrate due to the good dispersion in absolute ethanol. The thickness of QD-Siloxene nanosheets we prepared is 1.028 nm as shown in Figure 3c (Figure S3, Supporting Information), similar to graphene. We have measured multiple data and found that the thickness of nanosheets is almost 1~2 nm, corresponding to less than five atomic layers of silicon, which demonstrates that the sample consists of few-layer siloxene nanosheets.¹ The presence of raised silicene quantum dots can also be observed from the AFM image and thickness data. The silicene quantum dots in the siloxene nanosheets have an unusual anti-oxidant property, unlike other Si nanomaterials, the reason of which may be that the silicene quantum dots are protected by the surrounding amorphous structure, meaning that the QD-Siloxene can be exposed to air for a long time.^{19, 39}

The three types of layered siloxene can be broken into nanosheets uniformly dispersed in absolute ethanol via ultrasonic treatment. The morphology of the obtained siloxene nanosheets is clearly shown in the transmission electron microscope (TEM) images (Figure 3d-e, Figure 4 and Figure S2c-f, Supporting Information). Since the prepared nanosheets are ultra-thin, the contrast between the nanosheets and the ultra-thin carbon film of the carbon coated TEM grid is not obvious. We have used the copper TEM grid coated with CNTs as the support material for TEM test. Figure S2b shows a TEM image and a selected area electron diffraction (SAED) pattern of carbon nanotubes (CNT) coated on the copper TEM grid, in order to eliminate the interference of carbon nanotubes on structure characterization of the samples. The carbon nanotubes exhibit a polycrystalline structure with diffraction rings marked by red dashed lines in SAED images. Figure 3d shows a typical scanning transmission electron microscopy (STEM) image of QD-Siloxene nanosheets absorbed on the carbon nanotubes, which shows that the nanosheets are almost transparent, with very thin thickness, indicating the high degree of exfoliation. The TEM images of HCl-Siloxene and EAC-Siloxene nanosheets (Figure S2c-f, Supporting Information) show that the bulk CaSi₂ are divided into ultrathin nanosheets after exfoliation, including some amount of fragments, and the thickness of which is thicker than that of the QD-Siloxene. High resolution transmission electron microscopy (HRTEM) measurements are performed to investigate the interior structure of the three types of siloxene nanosheets. Figure 3e shows the distribution of the

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silicene quantum dots confined in the QD-Siloxene nanosheets, indicating that the silicene quantum dots are uniformly distributed on the siloxene nanosheets, and the diameter of which is about $2\sim5$ nm. Statistical analysis by selecting more than 200 quantum dots to measure their diameters shows that the majority of silicene quantum dots fall within the narrow range of 2-3 nm, with an average diameter of 2.5 nm, as shown in the core-size histogram (Figure 3f). Few research has been able to prepare silicene quantum dots and obtain such a precise distribution before. In previous research, organically functionalized silicene quantum dots have been synthesized by chemical exfoliation of calcium silicide and stabilized by hydrosilylation with olefin/acetylene derivatives forming Si-CH₂-CH₂- or Si-CH=CH- interfacial bonds, preparing the silicene quantum dots with the average diameter of about 2 nm, but the thickness is approximately 3.5 nm due to the octyl ligand.⁵ In our experiment, Si can spontaneously assemble at the defects of nanosheets under the combined action of ethyl acetate and FeCl₃, presenting a crystalline state. When the growth time is controlled to be consistent, the difference in the size of silicon-rich regions is small, obtaining a relatively uniform size distribution.



Figure 4. a-b) HRTEM images and selected area electron diffraction (SAED) patterns of silicene quantum dots with different sizes confined in the QD-Siloxene nanosheets. c) HRTEM images and SAED patterns of the thick stacking region in QD-Siloxene nanosheets.

The selected area electron diffraction (SAED) patterns show the polycrystalline structure of the silicene quantum dots (Figure 4), taken with the electron beam perpendicular to the surface of the nanosheets. As the diameter of the silicene quantum dots increases, the diffraction spots change from disorder to order. Compared to the silicene quantum dots with smaller diameter (≈ 2.5 nm), the silicene quantum dots with larger diameter (≈ 5 nm) are of better crystallization, and the lattice fringes are more clear. By calibrating the SAED patterns (Figure 4a-b), it is proved that the crystal structure of the quantum dots increase, the crystal structure gradually becomes the tetragonal phase (PDF#39-0973). Therefore, the SAED results indicate that the crystal structure of the silicene quantum dots confined in QD-Siloxene nanosheets is gradual. In the high-resolution TEM

(HRTEM) images of Figure 4b and Figure S7, it is easy to identify crystalline nanodomains with size of about 5 nm, which are well wrapped by amorphous matrix. According to the crystallographic parameters of PDF#41-1111, it can be judged whether the dots are silicene quantum dots by the SAED pattern. The crystal structure of the silicon dots is cubic, while the structure of silicene dots is layered structure with a interplanar spacing of 2.2Å. By indexing the SAED patterns, the interplanar spacing is 2.2 Å, which is consistent with that of the silicene quantum dots (PDF#41-1111), different from that of the crystal silicon quantum dots (3.1 Å).³⁹ It is noticed that the darker colored dots observed in STEM and HRTEM images corresponds to the non-smooth surface of the ultra-thin nanosheets shown in the AFM image. The thickness of the nanosheets is about 1.5 nm, corresponding to less than five atomic layers of silicon, and the structure of crystalline quantum dots is not cubic, indicating that the dots are few-layer 2D structure. Crystalline silicon nanosheets can be found in the thick stacking region of QD-Siloxene nanosheets. The HRTEM image and SAED pattern show the interplanar spacing of the nanosheets is 2.7 Å, corresponding to the d (130) planes of tetragonal phase Si (PDF#39-0973), as shown in Figure 4c. The result indicates that the topochemical reaction of CaSi₂ in ethyl acetate can synthesize crystalline silicon nanosheets due to the stacking of the 2D corrugated Si planes. However, the nanosheets with the thickness below about 2.5 nm are severely oxidized. Figure S2d shows the typical HRTEM image of EAC-Siloxene nanosheets, indicating that there are some silicon-rich regions in the siloxene nanosheets. There are no obvious diffraction spots or rings in the SAED image after the diffraction rings of the carbon nanotubes are excluded, indicating that the EAC-Siloxene nanosheets are amorphous. It is difficult to form the silicon-rich regions into crystalline silicene quantum dots in ethyl acetate without FeCl₃. The HRTEM and SAED results of HCl-Siloxene nanosheets exhibit uniform and homogeneous contrast of the nanosheets, without

obvious diffraction spots or diffraction rings (Figure S2f, Supporting Information), indicating that the siloxene nanosheets synthesized directly by hydrochloric acid are amorphous. The results indicate that the siloxene nanosheets prepared only by hydrochloric acid are amorphous silicon oxide, and the pre-decalcification process by ethyl acetate forms silicon-rich regions in the siloxene nanosheets, without crystalline silicene quantum dots. When FeCl₃ is used as the oxidant, the silicon-rich regions are converted into silicene quantum dots, and the quantum dots have gradual crystal structures due to the difference of initial enrichment.

The optical properties of the three types of siloxene nanosheets are characterized by the UVvisible absorption (UV-vis) and photoluminescence (PL) measurements. Figure 5a shows the UVvis absorption spectrum of the siloxene nanosheets dispersed in ethanol, indicating that OD-Siloxene has two absorption peaks at about 240 nm and 358 nm, while the absorption profiles of HCl-Siloxene and EAC-Siloxene are almost featureless. Due to the thick two-dimensional Si planes stacking crystal structure, the absorption peak of QD-Siloxene at 240 nm corresponds to a direct transition at the Γ point ($\Gamma_{25} \rightarrow \Gamma_{2'}$) or possibly the direct transition at X in the silicon nanocrystal with a size of 8-10 nm.⁴⁷ The peak at 358 nm (3.5 eV) is related to the direct transition at the Γ point ($\Gamma_{25} \rightarrow \Gamma_{15}$) which is similar to previous research of the bulk Si (365 nm, 3.4 eV).⁴⁶ The silicon nanocrystal with a size of 8-10 nm has significant peaks in the UV-vis absorption spectrum, but since this size is comparable to the size of the excitonic diameter in bulk Si, with almost no quantum confinement effects, the nanocrystal has no obvious photoluminescence properties.⁴⁷ Referring to previous reports, the energy difference of about 1 eV in the absorption spectrum may be associated with the thickness of the nanosheets.²⁹ HCl-Siloxene and EAC-Siloxene dispersed in ethanol mainly exist in the form of silicon oxide, and the large-particle silicon crystal formed by stacking during the topochemical reaction precipitates in the solution,

thus there are no obvious characteristic absorption peaks in the UV-vis absorption spectrum. The optical bandgap of about 3.14 eV (absorption edge at about 395 nm) is consistent with the estimated direct bandgap of 3.1 eV.⁴⁵ Calculate the optical bandgap (E_g) of the QD-Siloxene based on the UV-vis absorption spectrum (Figure S4, Support Information), linearly extrapolating to zero to obtain the optical bandgap, which includes a direct transition (E_d =3.01 eV) and an indirect transition (E_i =2.37 eV) respectively, and both are larger than that of bulk silicon crystal (1.1 eV). The PL emission of QD-Siloxene at 435 nm is matched to the optical bandgap for the direct transition of about 3.01 eV (Figure 5b), identical to the previous reports on the photoluminescence of two-dimensional silicon nanocrystal, indicating that the blue emission at 435 nm is from silicene quantum dots, which shows the conversion from indirect transition to quasi-direct transition of the silicon crystal.⁴⁶



Figure 5. a) UV-vis absorbance spectrum of the products. b) Room-temperature PL spectra of QD-Siloxene nanosheets powders (325 nm excitation). The blue emission at 435 nm is similar to

the optical band gap for the direct transition (3.01 eV) as calculated from the absorbance measurements. c) Room-temperature PL spectrum of the products (325 nm excitation). d-e) Time-resolved PL spectrum of QD-Siloxene (375 nm excitation). The decays are recorded at emission wavelengths of d) 435 nm and e) 465 nm, respectively. f) The strong blue emission of QD-Siloxene nanosheets powders can be observed by the naked eye when exposed to UV light.

Figure 5c shows the PL spectra of the siloxene nanosheets powders, with an excitation wavelength of 325 nm, the strong blue emission of QD-Siloxene observed by the naked eye (Figure 5f). The PL spectrum of the QD-Siloxene (red, solid) shows broad peaks at 435 nm (2.85 eV) and 465 nm (2.67 eV), showing that there are multiple luminescence mechanisms in nanosheets. The emission peak at 435 nm corresponds to the absorption edge of 2D Si nanosheets in the UV-vis spectrum, which is very close to the emission peak at 434 nm in the reference, indicating that twodimensional silicon backbone is maintained because the PL of the silicon quantum dots, with diameters smaller than 2 nm, has a peak at 3 eV.²⁹ The PL spectrum of HCl-Siloxene (black, solid) shows a single luminescence peak at 485 nm, while the spectrum of EAC-Siloxene (blue, solid) shows two peaks at 390 nm and 465 nm. The radiative lifetime of the nanosheets is calculated by time-resolved PL (TR-PL) measurement (excitation wavelength=375 nm), in order to analyze the luminescence mechanisms in combination with the results of PL spectroscopy, as shown in Figure 5d-e and Figure S5. The TR-PL spectrum of QD-Siloxene nanosheets shows that the luminescence at an emission wavelength of 435 nm has a single radiative lifetime of about 1.098 ns and a biexponential decay at 465 nm, the lifetime of which has two components, 8.291 ns and 1.141 ns, respectively (Figure 5d,e).

Based on the research of the luminescence mechanism of 2D Si nanostructures, there are mainly three possible mechanisms for the blue emission: band-edge emission caused by band-to-band

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recombination in silicon nanocrystals, emission from the oxide, and emission due to surface states and interface states.⁴⁸ Most of the silicene quantum dots confined in QD-Siloxene nanosheets have a size of about 2.5 nm as shown in the HRTEM images. Due to the band gap broadening caused by quantum confinement effects, when the size of silicon crystal is smaller than its exciton Bohr radius (~ 5 nm), the photoluminescence is generated by band-to-band radiation transition, and the decrease of size results in the blue emission. The UV-vis absorption spectrum of the band-to-band recombination shows a significant absorption edge, and the PL spectrum shows an illuminating peak near the band gap. The energy of both is close to the forbidden band width, thus the luminescence mechanism is attributed to the quasi-direct band transition of silicene quantum dots, corresponding to the emission peak at 435 nm of QD-Siloxene. For the quantum confinement effects, the band gap of the nano-silicon is widened and the single radiative lifetime becomes shorter as the size of the nano-silicon decreases. In our experiments, the crystal structure of the silicene quantum dots confined in few-layer siloxene nanosheets shows low-buckled 2D nanostructure formed by interconnected Si₆ rings, belonging to a type of quasi-zero-dimensional material, resulting in more significant quantum confinement effects and shorter single radiative lifetime than silicon quantum dots. In the characterization of EAC-Siloxene, it is noticed that its blue light emission peak is at 465 nm. Since there are no silicene quantum dots confined in EAC-Siloxene nanosheets, and the decay of QD-Siloxene and EAC-Siloxene at 465 nm is biexponential, previous studies have shown that it is mainly due to the oxygen-related surface states and defects.^{49,} ⁵¹⁻⁵² Because of the siloxene planes and silicon-rich regions (silicene quantum dots), there are many oxygen defects, interface states and surface states in the nanosheets. In the silicon-rich siloxene, silicon will be deeply recombined with the surrounding oxygen defects, leading to deep transition luminescence, which belongs to near-band edge emission. This luminescence mechanism is

attributed to the direct radiative recombination, with extremely short lifetime (~ 1 ns), thus corresponding to the short lifetime component in the TR-PL measurement.⁵⁰ The long lifetime component is mainly from the traps associated with some surface states and interface states.⁴⁹⁻⁵⁰ In the silicon-rich regions of the nanosheets, the bound excitons are first transferred to the local surface states and interface states without radiation under thermal activation, and then relaxes to the ground state, which has a longer radiative lifetime (>5 ns). The luminescence peak of EAC-Siloxene at 390 nm may be caused by the defects of peroxy bond, which is derived from the topochemical reaction in ethyl acetate without FeCl₃.¹⁸ A particular PL luminescence peak at 485 nm is observed in HCl-Siloxene nanosheets with a radiative lifetime of 1.086 ns, due to the presence of a large number of Si-OH functional groups on the surface of HCl-Siloxene. As numerous Si-OH functional groups exist, the blue-PL band moves slightly to longer wavelengths.⁴⁸ Therefore, the peak of HCl-Siloxene derived from Si oxides is red-shifted due to the same deep recombination from oxygen deficiency, with a short radiative lifetime. In addition, since the HCl-Siloxene nanosheets are relatively uniform and have no obvious silicon-rich regions, result in less interface states and the surface states from uneven areas, there is almost no long lifetime component, exhibiting a single radiative lifetime.

3. Conclusion

In summary, we have prepared silicene quantum dots confined in few-layer siloxene nanosheets at room temperature by a simple topochemical reaction method, and reported their structural and optical properties. In this work, FeCl₃•6H₂O is used as the oxidant and ethyl acetate is used as the reaction solvent, both of which promote the self-organized process of silicene quantum dots. Microscopic and XRD measurements have indicated that the QD-Siloxene nanosheets are mainly composed of amorphous siloxene, and silicene quantum dots with a diameter generally less than 5

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nm are protected in the amorphous structure, showing anti-oxidant property. The synthesized nanosheets exhibit strong blue emission at room temperature and show a quasi-direct band transition characteristic, indicating that the band gap transforms due to the quantum confinement effects, which is important for the research and development of silicon optoelectronics. In addition, due to the simple and low-cost synthesis method, large-scale production of the QD-Siloxene nanosheets can be easily realized, showing great application prospects for the emitting layer materials of blue light-emitting diodes.

4. Experimental Section

4.1. Materials preparation

CaSi₂ (Sinopharm Chemical Reagent Beijing Co., Ltd) and FeCl₃•6H₂O (99%, Aladdin) were used in this study, and all the chemicals were not further purified. Silicene quantum dot-free siloxene nanosheets (HCl-Siloxene) were synthesized in the presence of hydrochloric acid. At air atmosphere, $CaSi_2$ (0.2 g) was mixed with hydrochloric acid aqueous solution (2 mol·L⁻¹, 20 mL) for 24 hours at room temperature (decalcification step). Partially silicon atoms aggregated siloxene nanosheets (EAC-Siloxene) were synthesized in anhydrous ethyl acetate. CaSi₂ (0.2 g) was mixed with ethyl acetate (20 mL) for 24 hours at room temperature (decalcification step). Siloxene nanosheets containing silicene quantum dots (QD-Siloxene) were synthesized in ethyl acetate, which utilized FeCl₃ as oxidant. CaSi2 (0.2 g), and FeCl₃•6H₂O (0.54 g, mole ratio=1:1) were mixed with ethyl acetate (20 mL) for 24 hours at room temperature (decalcification step). Since the three types of experiments have the same steps (acid-washing, centrifugation, sonication, drying and so on) after the decalcification step, we have combined the same experimental step descriptions in the following. All the obtained products were centrifuged, and then added with hydrochloric acid aqueous solution (2 mol \cdot L⁻¹, 25 mL). The mixture was acid-washed for 3 hours to remove impurities such as unreacted CaSi₂. Then, the products were rinsed with ethanol and centrifuged for few times, followed by sonicating for 2 hours in ethanol to reduce the interaction between nanosheets. After sonication, the products were centrifuged at low speeed and then the upper mixed solution was collected, followed by drying in vacuum at 60 °C. In addition to the target product, the by-products mainly include large-particle nano silicon, silicon oxides formed by agglomeration and a trace amount of iron-containing compound impurities.

4.2. Structural characterization

The crystal structures were determined by X-ray diffraction (XRD). XRD characterization was performed using a X'pert PRO system (PANalytical) operated at 40 keV and 40 mA, equipped with a Cu K α radiation source (λ =1.5406 Å). Transmission electron microscopy (TEM) and highresolution TEM (HRTEM) observations on the siloxene nanosheets were conducted using a Philips-FEI Tecnai G2 F30 S-Twin operated at 200 KeV. STEM images were collected on a Philips-FEI Tecnai G2 F30 S-Twin operated at 200 KeV. The siloxene nanosheets were transferred by drop-casting the solution onto carbon nanotube (CNT) coated copper TEM grids. The morphologies and microstructures of the siloxene nanosheets were observed by scanning electron microscopy (SEM, Hitachi S-4800). The thickness of siloxene nanosheets was determined by AFM (AFM, Bruker Vecco, and Oxford Cypher S). Raman spectra were acquired with a laser confocal Raman spectrometer (LabRAM HR Evolution) using a wavelength of 532 nm. The Fourier transformed infrared spectra (FTIR, Tensor 27) were collected from 400 to 4000 cm⁻¹. The oxidation state of Si in siloxene nanosheets was identified using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). XPS core level spectra were acquired using Al Ka radiation (1486.6 eV) as the excitation source, and the binding energy was calibrated with C1s (284.8 eV) of adventitious carbon in the vacuum chamber.

4.3. Optical Characterization

Ultraviolet–visible (UV–vis) absorption spectra of siloxene nanosheets were collected on an Agilent Cary 60 UV–vis Spectrometer. The steady-state and time-resolved photoluminescence (PL) spectra were recorded by using a FLS920 fluorescence spectrometer (Edinburgh Instruments). A pulsed laser diode with a wavelength of 404.2 nm and a pulse width of 58.6 ps was used as the excitation light source. The highest excitation fluence was 4 nJ•cm⁻². PL transients were measured by the standard time-correlated single-photon counting (TCSPC) technique.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge.

Additional XPS, SEM, TEM, AFM, Time-resolved PL and XRD test. (PDF)

AUTHOR INFORMATION

Corresponding Author

* Email: huangjy@zju.edu.cn (JY Huang), yezz@zju.edu.cn(ZZ Ye)

Author Contributions

Xinling Xu, Liping Zhou, Degong Ding, Yang Wang, Jingyun Huang,* Haiping He, and Zhizhen Ye*

Notes

The authors declare no competing financial interest.

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