Two-dimensional gersiloxenes with tunable bandgap for photocatalytic H2 evolution and CO2 photoreduction to CO

Fulai Zhao1, Yiyu Feng1,2✉, Yu Wang1, Xin Zhang1, Xuejing Liang1, Zhen Li1, Fei Zhang1, Tuo Wang3,4, Jinlong Gong3,4 & Wei Feng1,2,4✉

The discovery of graphene and graphene-like two-dimensional materials has brought fresh vitality to the field of photocatalysis. Bandgap engineering has always been an effective way to make semiconductors more suitable for specific applications such as photocatalysis and optoelectronics. Achieving control over the bandgap helps to improve the light absorption capacity of the semiconductor materials, thereby improving the photocatalytic performance. This work reports two-dimensional −H/−OH terminal-substituted siligenes (gersiloxenes) with tunable bandgap. All gersiloxenes are direct-gap semiconductors and have wide range of light absorption and suitable band positions for light driven water reduction into H2, and CO2 reduction to CO under mild conditions. The gersiloxene with the best performance can provide a maximum CO production of 6.91 mmol g−1 h−1, and a high apparent quantum efficiency (AQE) of 5.95% at 420 nm. This work may open up new insights into the discovery, research and application of new two-dimensional materials in photocatalysis.
Photocatalysis has attracted wide attention due to the high efficiency, low energy consumption, clean, and non-photocatalytic advantages. 2D nanomaterials provide a wide range of opportunities for constructing diverse forms of composite photocatalysts with high activity for photocatalysis, due to their extraordinary advantages such as the atomic thickness, larger surface-to-volume ratio, good conductivity, superior electron mobility, and the high fraction of coordinated unsaturated surface sites. However, the important properties that qualify a 2D crystal for photocatalytic application are the suitable bandgap, band edge levels, optical absorption, and charge carrier mobility. Most 2D materials have several structural limitations as photocatalysts, for example, graphene is zero-bandgap material, which is not sufficient to absorb light to drive photocatalytic oxidation or reduction reaction; the absorption range of g-C3N4 is mainly limited in the ultraviolet region; the monolayer of transition-metal chalcogenides represented by MoS2 and WS2 is direct-bandgap semiconductor, while the bilayer and multilayer are indirect semiconductors, which will affect the energy conversion efficiency of light. In addition, most 2D semiconductor photocatalysts need a noble-metal cocatalyst to improve the photocatalytic efficiency.

Silicene and germanene are group-IV 2D-Xenes analog to graphene, and are also the so-called zero-bandgap materials but with direct bandgap of 1.55 and 23.9 meV, respectively. They have better tunability of the bandgap and electronic structure, optical properties can be tuned to realize enhanced optoelectronic properties and photocatalysis applications. However, the creation of siligenes and their derivatives have rarely been reported. The synthesis of 2D Ge/Si alloy analogs of germanane and silicane would allow a better understanding of how the electronic structure, optical properties can be tuned to realize enhanced optoelectronic properties and photocatalysis applications.

In the study, we report the freestanding siligenes terminated with −H−OH (Ge1−xSiH1−x(OH)x, x = 0.1−0.9) and name them gersiloxenes, which are synthesized by the topochemical transformation of freestanding CaGe2−xSi2 alloys prepared by annealing stoichiometric ratios of calcium, germanium and silicon. By combining the experimental results with theoretical calculations, we demonstrate their direct gap type and the bandgap dependence on x (the content of Si), which increase with x values from 1.8 to 2.57 eV. The as-synthesized gersiloxene with x = 0.5 (HGeSiOH) is most suitable for photocatalytic hydrogen production and reduction of CO2 to CO than the silicene, germanane, or other gersiloxene samples due to its moderate band edge levels and bandgap, hybridized orbital composition of the valence band (VB) and conduction band (CB), wide spectral response range, high specific surface area, and oxygen vacancies in gersiloxenes. This gersiloxene generates H2 at a rate of 1.58 mmol g−1 h−1 in photocatalytic water reduction and CO as the product at a rate of 6.91 mmol g−1 h−1 in CO2 photoreduction under mild conditions (25 °C, 1 atm CO2) and without additional noble-metal cocatalysts.

Results
Characterization of the resulting materials. The synthesis of gersiloxenes was accomplished by the typical topotactic deintercalation of the Zintl-phase precursor CaGe2−xSi2 alloys (x = 0.1, 0.3, 0.5, 0.7, and 0.9). Crystals of CaGe2−xSi2 alloys were synthesized by sealing stoichiometric amounts of Ca, Ge, and Si inside a quartz tube at temperature of 1000−1200 °C. The as-prepared CaGe2−xSi2 alloys are bright black crystals with metallic luster and have stacking lamellar microstructure (Supplementary Figs. 1, 2, details in Supplementary Note 1). X-ray diffraction (XRD) patterns (Supplementary Fig. 3) demonstrated they have the same trigonal rhombohedral tr6 crystal structure as that of CaSi2 and CaGe2. The lattice constant a gradually changes from 3.9837 to 3.8613 Å as x increases from 0.1 to 0.9 (Supplementary Table 1), following the Vegard’s law (details in Supplementary Note 1). These Zintl-phase CaGe2−xSi2 alloys were converted into 2D Ge1−xSiH1−x(OH)x (x = 0.1−0.9) by topotactic deintercalation in aqueous HCl at −30 °C for 3−10 days. Based on subsequent structural characterization, we present a schematic diagram of the transformation, as shown in Fig. 1a. With x ≈ 0.5, the conversion of 2D CaGe2−xSi2 alloys to Ge1−xSiH1−x(OH)x is similar to that of CaGe2−xSn2 alloys into 2D Ge1−xSn1−x(OH)x (x = 0−0.09) because the Si−O−Si bond (800 kJ mol−1) is much stronger than the Ge−O−Ge (660 kJ mol−1), Ge−H (320 kJ mol−1), and Si−H bonds (300 kJ mol−1). Moreover, Ge−O bonds can be readily cleaved in hydrochloric acid, thereby forming 2D GeSi alloys terminated with Ge−H and Si−OH that are connected to honeycomb GeSi planes, i.e., (GeH)y(SiOH)x, when x ≈ 0.5, Si−H bonds appeared; therefore, every Ge atom is terminated with −H, and Si atoms are terminated with either −H or −OH above or below the layer, i.e., forming (GeH)y(SiOH)xH2−y.O.5. The overall topochemical transformation reactions are as follows:

\[
\text{CaGe}_2-x\text{Si}_2 + 2\text{HCl} + x\text{H}_2\text{O} \rightarrow 2(\text{GeH})_{1-x}(\text{SiOH})_x \quad (1)
\]

\[
\text{CaGe}_2-x\text{Si}_2 + 2\text{HCl} + x\text{H}_2\text{O} \rightarrow 2(\text{GeH})_{1-x}(\text{SiOH})_{0.5}\text{H}_2O \quad (2)
\]

XRD patterns of the as-prepared products (Fig. 1b) obtained from the topotactic deintercalation of CaGe2−xSi2 alloys showed a diffraction structure similar to that of GeH9,24 and SiH2(OH)3 and no phase separation of the Ge1−xSiH1−x(OH)x alloys into the pure phases GeH and SiH2(OH)3. Samples with x = 0.1 and 0.3 showed the 6R phase typical of GeH, while for x = 0.5, 0.7, and 0.9, the samples exhibited the same 1T phase as that of SiH2(OH)3. The major diffraction peaks at ~15–16° and 26–28° were indexed to the (000) and (012) planes (for x = 0.1 and 0.3) or (001) and (100) (for x = 0.5, 0.7, and 0.9) respectively. It can be seen that with increasing x values, the angle of 2θ corresponding to the (000) or (001) crystal plane decreases gradually, while the corresponding interplanar spacing increases gradually. This phenomenon was caused by the increase in Si content together with the −OH termination, which was conducive to larger interlayer spacing. The angle of 2θ corresponding to the (012) or...
The weak doublet peak at 780 and 845 cm⁻¹ and Si₆H₃(OH)₃ are apparent that the number of layers in the samples with x = 0.5 and x = 0.7 is significantly less than that in the other samples because their transparency and wrinkles are significantly greater. High-resolution transmission electron microscopy (HRTEM) images showed clear lattice fringes, and selected area electron diffraction (SAED) patterns of samples exhibited two sets of hexagonally arranged diffraction fringes, and selected area electron diffraction (SAED) patterns of the topotactic deintercalation products gersiloxenes with varying x (x = 0.1, 0.3, 0.5, 0.7, 0.9), GeH and Si₆H₃(OH)₃. XRD, X-ray diffraction. Source data are provided as a Source Data file.

Figure 2 showed TEM images of as-prepared Ge₁−ₓSi₁−ₓH₁−ₓ(OH)ₓ. All the samples had a graphene-like layered morphology with wrinkles similar to that reported for GeH and Si₆H₃(OH)₃. It is also apparent that the number of layers in the samples with x = 0.5 and x = 0.7 is significantly less than that in the other samples because their transparency and wrinkles are significantly greater. High-resolution transmission electron microscopy (HRTEM) images showed clear lattice fringes, and selected area electron diffraction (SAED) patterns of samples exhibited two sets of hexagonally arranged diffraction spots, revealing the high-quality crystalline structure of 2D Ge₁−ₓSi₁−ₓH₁−ₓ(OH)ₓ. From the HRTEM images, we can observe that the crystal spacings of d₁₂₀=0.1, d₁₂₀=0.3, d₁₀₀=0.2, d₁₀₀=0.7, d₁₀₀=0.9 were 0.334, 0.330, 0.322, 0.326, and 0.318 nm, respectively, which match well with the powder XRD patterns. Atomic force microscope (AFM) was used to confirm the several atomic layer thickness of 2D gersiloxenes. As shown in Fig. 3, the thickness of the nanosheets was measured to be ~3−6 nm.

Fourier transform infrared (FTIR) spectroscopy was used to confirm the chemical structure of the as-prepared 2D gersiloxenes. For comparison, GeH showed extremely strong Ge−H stretching at ~2000 cm⁻¹ and multiple wagging modes at 570 and 479 cm⁻¹. The weak doublet peak at 780 and 845 cm⁻¹ is due to GeH₂ bending modes from neighboring Ge atoms at the edges of each crystalline germanane sheet. For Si₆H₃(OH)₃, the bands observed at 519, 640, 876, 1056, 1638, and 3406 cm⁻¹ correspond to the vibrations of ν(Si−O), δ(Si−H), ν(Si−OH), ν(Si−O), ν(Si−H), ν(Si−O), ν(Si−H), ν(Si−O), ν(Si−H) respectively. It can be seen from the FTIR spectrum (Fig. 4a) of 2D gersiloxenes (with x values from 0.1 to 0.9) that the vibration peaks of Ge−H stretching and Si−OH stretching always exist regardless of the value of x. With increasing x value, the Ge−H bond shifted to high wavenumbers. This shift is caused by Si−OH groups, as the Si−OH group exhibits a stronger dipole moment than the Si−H group, thus affecting the stretching vibration of Ge−H groups on adjacent germanium atoms. Moreover, the vibration peak of Si−H stretching only appears when x > 0.5, and the intensity ratio of the Si−H to Ge−H vibration peaks increases with the x value. The Si−Si stretching vibration peak also becomes more prominent than that of the Ge−H wag when x > 0.5. Raman spectroscopy was employed to further study the chemical structure of 2D gersiloxenes. As shown in Fig. 4b, peaks at 281−292 cm⁻¹, 484−495 cm⁻¹, and 388−413 cm⁻¹ can be attributed to the phonon modes of Ge−Ge, Si−Si and Ge−Si bonds, respectively. Peaks at ~640 and ~730 cm⁻¹ can be assigned to Si−H bonds, and broad peaks at ~2100 cm⁻¹ are assigned to Si−H₂, which is present only at the sides of silicon nanosheets. It is known that crystalline Ge and Si exhibit Raman peaks at 300 and 520 cm⁻¹ that correspond to Ge−Ge bonds and Si−Si bonds, respectively. Compared to those of the corresponding bonds in crystalline germanium and silicon, the Raman peaks of both the...
2D gersiloxenes. The XPS survey spectra showed that all 2D was performed to con small to be detected. X-ray photoelectron spectroscopy (XPS) the proportion of Si from Ge atoms (for which separate Si from atom by Ge atoms, due to the uniform distribution of GeSi atoms in the two systems, was not detected in the sample with increasing value. It is noteworthy that the vibrational mode of Si–H and Si–H peaks appears only when \(x \geq 0.5\), indicating that when \(x \leq 0.5\), only hydroxyl groups are bonded to Si, while when \(x > 0.5\), either hydrogen atoms or hydroxyl groups are bonded to Si. This finding is consistent with the FTIR results. Moreover, with the increase in \(x\) value, both the Ge–Ge and Si–Si peaks broadened, indicating that the crystallinity of the 2D gersiloxenes exhibits a slight decrease with increasing \(x\) value. It is noteworthy that the Si–Si bond was not detected in the sample with \(x = 0.1\) and that the Ge–Ge bond was not detected in the sample with \(x = 0.9\). This result may be due to the uniform distribution of GeSi atoms in the two systems, which separate Si from Si atoms by Ge atoms (for \(x = 0.1\)) or Ge from Ge atoms (for \(x = 0.9\)) by Ge–Si bonds. It may also be that the proportion of Si–Si or Ge–Ge bonds in the structure is too small to be detected. X-ray photoelectron spectroscopy (XPS) was performed to confirm the configuration of the as-prepared 2D gersiloxenes. The XPS survey spectra showed that all 2D Ge\(_{1-x}Si\(_{x}\)H\(_{y}\)(OH)\(_{z}\) samples contain elements of Ge, Si, O, and Cl (Fig. 4c). The high-resolution Ge3d XPS spectra exhibit peaks at ca. 30 eV, corresponding to the Ge–Ge bonds (Fig. 4d), and the shoulder peaks around 32.7 eV are ascribed to Ge–O bonds, which is due to the trace oxidation on the surface similar to that of germanium nanosheets\(^{30,31}\). In the Si2p spectra, the peaks are located at binding energies of approximately 99.9 and 103.0 eV, corresponding to Si–Si bonds and Si–O bonds in the two-dimensional Si chain network (Fig. 4e), respectively. By contrast, the Ge–Ge and Si–Si bonds for the precursor CaGe\(_2\)Si\(_{32}\) are located at 28.8 and 98.5 eV (Supplementary Fig. 4), respectively. This result indicates that CaGe\(_2\)Si\(_{32}\) transforms to 2D Ge\(_{1-x}Si\(_{x}\)H\(_{y}\)(OH)\(_{z}\)

Fig. 2 Morphology and structural characterization of gersiloxenes. a-e Low-magnification TEM images, f-j HRTEM micrograph, and k-o electron diffraction patterns of gersiloxenes sheets. a, f, k, x = 0.1; b, g, l, x = 0.3; c, h, m, x = 0.5; d, i, n, x = 0.7; e, j, o, x = 0.9. TEM transmission electron microscopy, HRTEM high-resolution transmission electron microscopy.
Fig. 3 Thickness characterization of gersiloxenes. AFM images and corresponding height profiles of gersiloxenes nanosheets. a $x = 0.1$. b $x = 0.3$. c $x = 0.5$. d $x = 0.7$. e $x = 0.9$. AFM atomic force microscope. Source data are provided as a Source Data file.
structure. Gersiloxenes with \( x = 0.1 \) and \( 0.3 \) had regular layered stacking structures with larger lamellar sizes. When \( x = 0.5 \), the size of the nanosheets decreases significantly, and the lamellae become fragmented. The gersiloxenes with \( x = 0.1 \) and \( 0.3 \) are regular and flat layered structures. However, as \( x \) increases to \( x = 0.5 \), the size of the lamellae decreases gradually. When \( x > 0.5 \), the size of the lamellae increases again. In addition, the structure of the gersiloxenes with \( x > 0.5 \) become distorted and strip or ribbon-like. As shown in Supplementary Fig. 6, SEM elemental mapping of all samples revealed a uniform distribution of Si, Ge and O. The corresponding energy-dispersive spectroscopy (EDS) results helped confirm that the Ge/Si ratios (shown in Table 1) in the as-synthesized 2D gersiloxenes are almost consistent with the intended \( x \) values. To investigate the influence of surface area, Brunauer–Emmett–Teller (BET) surface area measurements were carried out. The N\(_2\) Adsorption/desorption isotherms and pore-size distribution curves (Supplementary Fig. 7a–d) indicate that all gersiloxenes, GeH, and \( \text{Si}_6\text{H}_3\text{(OH)}_3 \) have mesoporous structure and gersiloxene with \( x = 0.5 \) exhibits the most extensive size distribution (details in Supplementary Note 2). Consistent with the differences between SEM images, the surface area continuously increases from 18.9 to 319.7 m\(^2\)g\(^{-1}\) for the \( x = 0.1 \) to \( 0.5 \) samples and then drops to 169.4 m\(^2\)g\(^{-1}\) as the \( x \) value increases to 0.9 (Table 1). In contrast, GeH and \( \text{Si}_6\text{H}_3\text{(OH)}_3 \) have
specific surface areas of 4.7 and 94.8 m² g⁻¹, respectively (Supplementary Fig. 7b). The aforementioned TEM results showed that the transparency and wrinkles of gersiloxene nanosheets with x = 0.5 is the most obvious of all gersiloxenes, indicating that the nanosheets with x = 0.5 is the best dispersed, and the interlayer agglomeration effect is the weakest among all samples. Moreover, SEM also showed that the overall size of gersiloxene nanosheets with x = 0.5 is significantly smaller than that of other gersiloxenes. These factors lead to the largest specific surface area, which can maximize its contact with the liquid. It is reported that the large specific surface area may be beneficial to improve the performance of photocatalysts, as it may provide a larger active area that offer paths for the migration of photogenerated carriers, promote the migration of photogenerated electrons and holes between layers, inhibit the recombination of carriers, and boost the release of generated gases.

Characterization by XRD, FTIR, Raman, XPS, SEM, BET, and TEM confirmed the chemical structural characteristics of the synthesized 2D honeycomb GeSi alloys and their physical properties of morphology and surface area. The optical properties of these 2D gersiloxenes were investigated by UV–vis diffuse reflectance spectroscopy (DRS). As shown in Fig. 5a, all gersiloxene samples have a wide range of light absorption from

| x       | 0.1 | 0.3 | 0.5 | 0.7 | 0.9 |
|---------|-----|-----|-----|-----|-----|
| Theoretical Ge/Si ratio | 9:1 | 7:3 | 1:1 | 3:7 | 1:9 |
| Experimental Ge/Si ratio detected by EDS | 8.44:1 | 8.89:3 | 11.07 | 3:6.36 | 18.77 |
| BET surface Area (m² g⁻¹) | 18.9 | 46.2 | 319.7 | 228.7 | 169.4 |

Table 1 Summary of the Ge/Si ratios and BET surface areas of 2D gersiloxenes with varying x values.

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Fig. 5 Optical properties and energy band structure of gersiloxenes. a UV–vis diffuse reflectance spectra and b Tauc plots of gersiloxenes (x = 0.1, 0.3, 0.5, 0.7, 0.9), GeH and Si₆H₃(OH)₃. c The optical images of GeH, Si₆H₃(OH)₃, and gersiloxenes with x = 0.1, 0.3, 0.5, 0.7, 0.9. d Energy band structure of gersiloxenes with different x values and GeH and Si₆H₃(OH)₃ for CO₂ reduction to CO and H₂ evolution. VB valence band, CB conduction band. Source data are provided as a Source Data file.
ultraviolet to visible light. The absorption range of gersiloxenes is between that of GeH and Si$_3$H$_3$(OH)$_3$. With the increasing $x$, the absorption edge shifts to the direction of short wavelength, which is consistent with the change in sample’s color from dark red, brick red, brown, yellow green, to light green (Fig. 5c). It is worth noting that gersiloxene shows obvious sub-bandgap absorptions compared with pure GeH and pure Si$_3$H$_3$(OH)$_3$. This sub-bandgap absorption is supposed to be caused by the oxygen vacancies, which is indicated by the XPS O1s spectra. Gersiloxene with $x=0.5$ exhibits the most significant sub-bandgap absorption, indicating that it has the highest oxygen vacancies concentration than other ones which may be attributed to its graphene-like 2D structure and the highest specific surface area among the as-synthesized gersiloxenes. The significant wide sub-bandgap absorption further increases the light absorption range of the material, which is advantageous for the enhanced photocatalytic and photoelectrochemical performance. Figure 5b presents the corresponding Tauc plots, which are calculated based on the assumption that the gersiloxenes are direct-bandgap semiconductor materials and proved by subsequent theoretical calculations. The bandgap values of GeH and Si$_3$H$_3$(OH)$_3$ are 1.53 and 2.45 eV, respectively, which is almost in agreement with the reports. For gersiloxenes, with an increasing $x$, the bandgap increased from 1.8 eV ($x=0.1$) to 2.57 eV ($x=0.9$), indicating that different $x$ values (the content of Si) endowed the 2D gersiloxenes with different bandgap and a wide adjustable absorption range that can be linearly regulated.

**Band structure analysis.** Based on the experimental results, we established a series of structural models (shown in Supplementary Fig. 8) to investigate the electronic band structure and partial density of states (PDOS) of the proposed 2D gersiloxenes (details in Supplementary Note 3). The theoretical calculations (Supplementary Figs. 9, 10) proved that the gersiloxenes are all direct-bandgap semiconductors. And the calculated bandgap values agree well with the experiments (Supplementary Fig. 11). The PDOS results suggest that the electronic states of the CB and VB near the Fermi level are hybridized by different orbitals of Ge and Si, O, and H (as summarized in supplementary Table 2 and Supplementary Table 3), which is beneficial for the migration of photogenerated electrons and can suppress the recombination of photogenerated electrons and holes. Moreover, the distribution of the valence band maximum (VBM) and conduction band minimum (CBM) for the gersiloxene with $x=0.5$ (i.e., HGeSiOH) is similar to that of type-II heterostructures, and the photoinduced electrons and holes would transfer to the CBM (Si) and VBM (Ge), respectively, which is more conducive to the separation of excited electrons and holes.

To determine the band positions of all samples, we investigated the VB positions of all samples by valence-band XPS (VB-XPS). As shown in Supplementary Fig. 12, the VB edge positions of samples with $x=0.1$, 0.3, 0.5, 0.7, and 0.9 are determined to be 0.84, 0.91, 1.14, 1.43 and 1.22 eV, respectively; whereas that of GeH and Si$_3$H$_3$(OH)$_3$ are 0.63 and 1.05 eV, respectively. According to the bandgap results obtained from DRS, the position of the conduction band maximum is calculated to be $-0.96,-1.04,-1.16,-1.10$, and $-1.35$ eV for gersiloxenes ($x=0.1$–0.9), respectively; for GeH and Si$_3$H$_3$(OH)$_3$, the calculated values are $-0.90$ and $-1.40$ eV respectively. The resulting electronic band structures are shown in Fig. 5d (The reaction energy levels for the transformation of CO$_2$ into CO and water reduction ($H^+$/H$_2$) and oxidation (O$_2$/H$_2$O) are taken from the literature[28]). It is obvious that the CB and VB energies of all gersiloxenes with different $x$ values meet the requirements of photocatalysts for hydrogen production and CO$_2$ reduction to CO. With increasing $x$, the CB position moves upward (becomes more negative), while the VB position moves downward (becomes more positive), which enables the gersiloxenes to more efficiently drive $H^+$ or CO$_2$ reduction and the oxidation of H$_2$O. For comparison, the energy band structure of GeH is not enough to satisfy the overall reaction conditions for water splitting or CO$_2$ reduction unless a sacrificial agent is used in the photocatalytic reaction process. Si$_3$H$_3$(OH)$_3$ can drive photocatalytic oxidation-reduction reactions, but its light absorption range is much smaller than that of GeH and HGeSiOH.

**Photoreduction activity of the resulting materials.** After successful synthesis of bandgap-tunable 2D gersiloxenes and illustration of their electronic structures, the photocatalytic capabilities of gersiloxenes were first evaluated by detecting their hydrogen evolution activity in water with the addition of sodium sulfite (0.10 M) as a sacrificial reagent. The $H_2$ evolution rates (HERs) were measured under 1 bar pressure and irradiation with a 300 W light source. Figure 6a shows the time-dependent photocatalytic hydrogen evolution for all gersiloxenes. As expected, the gersiloxene with $x=0.5$ exhibited a maximum yield of 9.50 mmol g$^{-1}$ for 6 h, corresponding to an HER of 1.58 mmol g$^{-1}$ h$^{-1}$, which is much higher than that of GeH and Si$_3$H$_3$(OH)$_3$. The HERs of gersiloxene increased with $x$ values from 0.17 ($x=0.1$) and 0.42 ($x=0.3$) to 1.58 mmol g$^{-1}$ h$^{-1}$ ($x=0.5$) and then decreased to 0.98 ($x=0.7$), and 0.78 mmol g$^{-1}$ h$^{-1}$ ($x=0.9$) (Fig. 6b). Cycling tests showed that the $x=0.5$ sample had stable activity for the production of hydrogen with little reduction in the hydrogen production rate (Fig. 6c). Furthermore, a photocatalytic CO$_2$ reduction performance test was conducted under an atmosphere with CO$_2$/H$_2$O. It was found that in a gas-liquid-solid reaction system, CO was the only direct product, and no other carbonaceous products or H$_2$ were detected. Comparison experiments were performed with no light irradiation, with no catalyst, and in the presence of N$_2$ gas. No carbonaceous products were detected (Supplementary Fig. 13), which confirmed that CO evolved from the photocatalytic effect of the gersiloxene in the mixture of CO$_2$ and H$_2$O (details in Supplementary Note 4). The trend of time-dependent photocatalytic CO evolution (Fig. 6d) is very similar to that of $H_2$ evolution. The gersiloxene with $x=0.5$ showed a maximal CO evolution rate (COER) of 6.91 mmol g$^{-1}$ h$^{-1}$ (Fig. 6e), in contrast, much higher than that of GeH (1.02 mmol g$^{-1}$ h$^{-1}$) and Si$_3$H$_3$(OH)$_3$ (1.51 mmol g$^{-1}$ h$^{-1}$). The COER of gersiloxene with $x=0.5$ is almost 691 times that of palladium-decorated silicon–hydride nanosheets (Pd@SiNS) tested under 170 °C in H$_2$/CO$_2$ atmosphere[29, 30] ~28 times that of surface hydride-functionalized silicon nanocrystals (ncSi:H)[57], and higher than overwhelming majority of the photocatalysts reported to date (Supplementary Table 5). And it maintained stable activity for 10 h (Fig. 6f). In addition, the apparent quantum efficiency (AQE) of gersiloxene with $x=0.5$ measured at different excitation wavelength shows a highest AQE of up to 5.95% at 420 nm (Supplementary Table 4 and Supplementary Fig. 14, details in Supplementary Note 5), which further indicating the high activity of photocatalyst.

The photogenerated carrier recombination and separation behaviors of 2D gersiloxenes were further investigated based on photoluminescence (PL) emission spectroscopy. It can be seen from Fig. 6g that all gersiloxenes have a wide range of fluorescence emissions in the range of 440–650 nm. The larger portion of emission signals at 440–530 nm is ascribed to the free exciton from electron–hole recombination. While the peak at 550–600 nm corresponded to the recombination of two-electron-trapped oxygen vacancies with photogenerated holes. In addition, the PL intensity shows an obvious decrease from $x=0.1$ to $x=0.5$ and a subsequent increase from $x=0.5$ to $x=0.9$. For
Holes, thus greatly improving the photocatalytic performance of gersiloxenes, GeH and Si6H3(OH)3. Photostability for H2 production of the gersiloxene with x = 0.9 (HGeSiOH). We also performed an electron spin resonance (ESR) test on the sample. ESR spectra (Supplementary Fig. 15a, b) indicate that HGeSiOH has abundant oxygen vacancies and changes little before and after illumination (This further explains the results of oxygen vacancies in XPS, UV, and the PL characterization). These holes may be caused by either Ge or Si atoms because oxygen vacancies are also present in GeH (caused by oxidation) and Si6H3(OH)3.Obviously, the concentration of oxygen vacancies in HGeSiOH is higher than that of GeH and Si6H3(OH)3. The presence of surface oxygen vacancy defects leads to electron enrichment, which enhances the activation of CO2 molecules, thereby further promoting CO2 reduction. Adsorption energies analysis. To further investigate the origins of the enhanced photocatalytic performance of the 2D HGeSiOH alloy, we performed DFT calculations of the adsorption energies (E_{ads}) of H2O and CO2 molecules at HGeSiOH, Si6H3(OH)3, and GeH surfaces because the adsorption capacity of a catalyst for H2O or CO2 is one of the most critical factors affecting photocatalytic performance.

Comparison, the PL intensity of GeH and Si6H3(OH)3 are much higher than that of the gersiloxene with x = 0.5. These results demonstrate that the gersiloxene with x = 0.5 has better capability to effectively suppress the carrier recombination than other gersiloxenes, GeH and Si6H3(OH)3. Thus, the extensive light absorption ability together with the less radiative electron–hole recombination endowed the gersiloxene (x = 0.5, HGeSiOH) with significantly enhanced photoactivity and photoelectrochemical performance. A photoelectrochemical test further confirmed that HGeSiOH shows the best photocurrent performance and the lowest interfacial resistance of charge carriers (Fig. 6h, i), coinciding with the HER and COER results. As HGeSiOH has the highest surface area of 319.7 m2 g−1, the distinctive two-dimensional nanostructure and large specific surface area of HGeSiOH provide more paths for the migration of photogenerated carriers, promote the migration of photogenerated electrons and holes between layers, and inhibit the recombination of carriers, thus greatly improving the photocatalytic performance of materials.

Fig. 6 Photocatalytic performance and electrochemical characterization. a, b Time-dependent photocatalytic hydrogen evolution (a) and HERs (b) of gersiloxenes with x = 0.1–0.9, GeH and Si6H3(OH)3. c Photostability for H2 production of the gersiloxene with x = 0.5 (HGeSiOH). d, e Time-dependent photocatalytic CO evolution (d) and COERs (e) of gersiloxenes with x = 0.1–0.9, GeH and Si6H3(OH)3. f Time-dependent photocatalytic CO evolution for 10 h. g–i PL spectra (g), EIS Nyquist plots (h) and transient photocurrent responses (300 W xenon lamp) (i) of gersiloxenes with x = 0.1–0.9, GeH and Si6H3(OH)3. HERs, H2 evolution rates. COERs CO evolution rates. PL photoluminescence, EIS electrochemical impedance spectroscopy. Source data are provided as a Source Data file.
hydrogen evolution and CO2 reduction performance. As Fig. 7a, b shows, the binding of H2O or CO2 to HGeSiOH and Si6H3(OH)3 was considered from two sides of the monolayer structures. For the Si–OH side of HGeSiOH and Si6H3(OH)3, the binding energies for H2O are −1.405 eV and −0.951 eV, respectively. For the other side of HGeSiOH and Si6H3(OH)3, the binding energies are −0.797 eV and −0.212 eV, respectively. The binding energy of H2O to GeH is −0.222 eV. Therefore, the interactions of an H2O molecule with the HGeSiOH, Si6H3(OH)3 and GeH surfaces are energetically favorable, and regardless of which side of the single-layer structure, the H2O adsorption energy on HGeSiOH is more negative than that on Si6H3(OH)3 and GeH, suggesting that the alloyed structure of 2D GeSi can significantly improve its H2O adsorption capacity. For CO2 adsorption, the binding energies to the Si–OH side of HGeSiOH and Si6H3(OH)3 are −0.750 eV and −0.270 eV, respectively. On the other side, the binding energies are −0.546 eV and −0.069 eV, respectively. The binding energy of CO2 to GeH is −0.121 eV, indicating that compared with 2D Si6H3(OH)3 and GeH, the alloy-structured 2D HGeSiOH has enhanced CO2 adsorption capacity. In addition, the calculation results show that the atoms closest to H2O and CO2 on HGeSiOH, Si6H3(OH)3, and GeH are H atoms from Ge–H and Si–OH bonds, Si–H and Si–OH bonds, and Ge–H bond, respectively. These findings indicated that both H2O and CO2 may be adsorbed and activated at the H and −OH sites and that −OH shows a better ability to interact with H2O and CO2 (the adsorption energies on the Si–OH side are more negative than those on the Si–H or Ge–H sides). One can clearly observe from the calculated results that Si–OH has a strong interaction with CO2 and H2O, while Si–H and Ge–H form weak coordination interactions with both CO2 and H2O. Therefore, it can be inferred that in the process of photocatalytic CO2 or H2O reduction, CO2 or H2O are mainly adsorbed and activated at the −OH site to obtain electrons and further reduced to H2 and CO. A comparison of adsorption energy calculated by different calculation software is presented in Supplementary Fig. 16 (details in Supplementary Note 6), and the conclusion is the same. The theoretical results align well with our experimental evidences in the fact that HGeSiOH showed better photocatalytic activity than that of GeH and Si6H3(OH)3.

In conclusion, we synthesized free-standing two-dimensional honeycomb-like Ge–Si alloy compounds (gersiloxenes) for the first time. The experimental results and theoretical calculations show that these two-dimensional compounds are all direct-bandgap semiconductors with tunable bandgaps ranging from 1.8 to 2.57 eV by increasing the Si content from 10 to 90%. In addition, the appropriate energy band position endows these materials with photocatalytic properties in H2O reduction to H2 and CO2 reduction to CO. The synthesized gersiloxene HGeSiOH (x = 0.5) has a relatively wide spectral response range and a suitable band position, which is most beneficial for the photogeneration of electrons and holes. The sample’s relatively higher specific surface area (319.7 m2 g−1) can provide more pathways for the migration of photogenerated carriers, which improves its photocatalytic performance. DFT calculations prove that the structure of HGeSiOH enhanced the material’s H2O and CO2 adsorption capacity, which is beneficial to the photocatalytic reaction. The hybridized orbital composition and distribution of the VB and CB for HGeSiOH are beneficial for the migration of photogenerated carriers and suppressing the recombination of photogenerated electrons and holes. Moreover, the presence of surface oxygen vacancy defects leads to electron enrichment and enhances the activation of CO2 molecules, facilitating the CO2 reduction. When used as a photocatalyst in water reduction to produce H2, it has a hydrogen production rate of 1.58 mmol g−1 h−1 and good cycle stability. When applied to photoreduction of CO2 under mild conditions (25 °C, 1 atm CO2), it achieves high conversion efficiency to produce CO with a production rate of 6.91 mmol g−1 h−1 and has a high AQE of 5.95% at 420 nm, which is better than the majority of recently reported photocatalysts. We believe that this research will provide many valuable references for the synthesis,
design, regulating electronic properties of new germanium/silicon-based two-dimensional materials and the development of their applications in photocatalysis.

**Methods**

**Synthesis of Ca$\text{Ge}_x\text{Si}_{2-x}$ crystals.** In a typical reaction, calcium (Ca, 99.9%, Aladdin), germanium (Ge powder, 99.999%, Macklin), and silicon (Si, 99.99%, Adamas) were loaded in stoichiometric amounts into a quartz tube and an argon-filled glovebox, then vacuum sealed using a MRVS-1002 vacuum sealing system (Partulab, Wuhan, China), annealed at 1000–1200 °C for 16–20 h with a tube furnace, and cooled to room temperature over 1–5 days.

**Synthesis of Ge$\text{Si}_x\text{H}_{2-x}$ (OH), Ca$\text{Ge}_x\text{Si}_{2-x}$ crystals were stirred in concentrated hydrochloric acid (HCl, AR, 37%) for 3–10 days at –30 °C under argon conditions. After that, the resulting products were transferred to a glove box filled with argon and filtered, followed by washing with Milli-Q H2O and isopropyl alcohol (IPA, CH$_3$CH$_2$OH, AR). Subsequently, the products were dispersed in IPA for 2 h of ultrasonic treatment and then centrifuged for 30 min at a speed of 1000 r·min$^{-1}$ to further exfoliate the stacked geroloxenes. Finally, the products were dried at room temperature on a Schlenk line and kept in an Ar-filled glovebox.

**Characterization.** Flat plane and capillary mode XRD was performed on a D8 Advanced X-ray diffractometer (BRUKER AXS GMBH) under Cu Ka radiation at a wavelength of 0.154 nm. The lattice parameters of the ZnI$_2$ phases were obtained through Rietveld analysis of the experimental data. FTIR was carried out on an FTIR 650 spectrometer (BRUKER AXS GMBH) with KBr discs. Raman spectra were acquired using a DLR Raman microscope from Thermo Scientific using a 532 nm laser source. Solid-state diffuse reflectance spectra (DRS) were recorded with a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer) by mixing samples thoroughly with barium sulfate (BaSO$_4$, SP, Rhawn) powder and spreading them evenly on a BaSO$_4$ background holder. The Kubelka-Munk remission function was employed to convert the measured reflectance to absorption. XPS measurements were performed at a power of 450 W using a PHI 1600 surface analysis system equipped with a Mg Kα anode. Field-emission scanning electron microscopy (FESEM) images were recorded by a Hitachi S-4800 field-emission Electron Microscope. Pt XPS spectroscopy was recorded with a Hitachi F-4600 fluorescence spectrophotometer at room temperature. For specific surface area measurements, nitrogen sorption analyses were carried out at 77 K for a P/$P_0$ of 0.025–0.3 with a Micrometrics ASAP 2050 analyzer (Micrometrics Instrument Corporation, Norcross, GA). A Dimension ICON-PT (BRUKER AXS GMBH) AEM was employed to investigate the morphology and thickness of samples. Low-temperature ESR spectra were collected using a BRUKER A300 ESR spectrometer (77 K, 9.063 GHz, X-band). A 300 W Xe lamp was used as a light source.

**Electrochemical analysis.** Electrochemical measurements were performed at room temperature on an electrochemical workstation (CHI 660d) with a three-electrode system. The working electrodes were prepared by dropping the sample slurry (5 mg dispersed in 200 μL of 0.5 wt% Na$_2$SO$_4$ electrolyte) on a 1.0 cm$^2$ PET ITO substrate and then drying in air at 80 °C. The electrode cell (using a 0.5 M Na$_2$SO$_4$ electrolyte) was used as the light source. The photocatalytic CO$_2$ reduction test. The photocatalytic activity of the catalyst at a specific excitation wavelength is obtained by a specific band pass filter ($\lambda$ = 380, 420, 525, 700 nm) with a 300 W Xe lamp in the same apparatus as the photocatalytic CO$_2$ reduction reaction. Generally, the AQE is calculated as follows:

\[
\text{AQE} (%) = \frac{n(\text{CO})}{I} \times 100%
\]

where $n(\text{CO})$ represents the number of molecules of CO production, and $I$ is the number of incident photons. In actual measurement, it is assumed that all incident photons are absorbed by the suspension; the calculation formula of the incident photon number $I$ is as follows:

\[
I = \text{PSt} \frac{\lambda}{\hbar v}
\]

where $P$ is the average intensity of the radiation (W/cm$^2$), $S$ is the incident irradiation area ($S$ = 19.63 cm$^2$), $t_\text{i}$ is the irradiation time (1 x 4 x 3600 s), $\lambda$ is the incident wavelength, $h$ is the Planck constant (6.626 x 10$^{-34}$ J·s), and $v$ is the speed of light (3 x 10$^8$ m/s$^{-1}$). Therefore, the calculation equation of AQE for photo-catalytic reduction of CO$_2$ to CO can be written as:

\[
\text{AQE} (%) = \frac{2CN}{PSt} \times \frac{100}{\lambda}
\]

where $C$ is the CO production amount (mol); $N_A$ is the Avogadro constant (6.02 x 10$^{23}$ mol$^{-1}$).

**Computational analysis for band structure.** Density functional theory (DFT) calculations were performed with the Vienna Ab initio Simulation Package (VASP) using the projector augmented wave (PAW) Perdew-Burke-Ernzerhof (PBE) pseudopotentials of the generalized gradient approximation (GGA). For monolayer structures, the calculations were performed in a fully relaxed manner, using the projector augmented wave (PAW) Perdew-Burke-Ernzerhof (PBE) pseudopotentials of the generalized gradient approximation (GGA). The Monkhorst-Pack k-point grid of (1 x 1 x 1) k points was used for electronic property calculations and geometry optimizations. The Heyd-Suesser-erzherzhof hybrid functional (HSE06) was used to calculate the band structures. The plane wave cutoff energy was set to 400 eV. For the two-layer unit cell of bulk structures, the optimizations were carried out until the maximum force upon each relaxed atom was $<0.01$ eV/Å and the energy convergence accuracy was $<10^{-5}$ eV. A Monkhorst-Pack grid of (11 x 11 x 1) k points was used for electronic property calculations and geometry optimizations. HSE06 was used to calculate the band structures, and the plane wave cutoff energy was set to 500 eV.

**Calculations of adsorption energy.** The interactions of HGeSiOH, Si$_2$H$_5$(OH)$_3$, and GeH with H$_2$O and CO$_2$ were calculated by DFT. The Dmol3 module in Materials Studio software was used for calculation. HGeSiOH, Si$_2$H$_5$(OH)$_3$, and GeH monolayer structures were all modeled as 4 x 4 superlattices, and the interlayer spacing between different layers was set to 20 Å to avoid the influence of interaction forces between different layers. In the process of structural optimization, the k-point of the Brillouin zone was set to 7 x 7 x 1. The GGA with the PBE functional was used as the exchange correlation function, the double numerical plus (DNP) polarization function was applied for the basis set of all the electrons, and the all-electron relativistic method was used to deal with the internal nuclear electrons. The convergence accuracy of the energy, maximum force and maximum displacement was set to 1 x 10$^{-5}$ Ha, 2 x 10$^{-3}$ Ha/Å (1 Ha = 27.2114 eV), and 5.0 x 10$^{-4}$ Å, respectively. Moreover, for comparison, we used VASP to perform the same calculations with the same superlattice size and the same k-points as used in the Dmol3 module in Materials Studio software, this would be helpful for the interest of relevant researchers. The simulated adsorption energies ($E_{\text{ads}}$) of H$_2$O and CO$_2$
molecules on HGeSiOH, Si₆H₆(OH)₂, and GeH surfaces were calculated by the following equation:

\[ E_{\text{ads}} = E_{\text{Total}} - (E_m + E_n) \]

where \( E_{\text{Total}} \) represents the total energy of H₂O or CO₂ adsorbed onto HGeSiOH, Si₆H₆(OH)₂, or GeH monolayers, \( E_m \) stands for the energy of pristine HGeSiOH, Si₆H₆(OH)₂, or GeH monolayers, and \( E_n \) stands for the energy of H₂O or CO₂ molecules.

### Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
F. Zhao, Y.F., and W.F. conceived the experiment. F. Zhao and Y.W. synthesized the CaGe2−xSi2x crystals and 2D gersiloxenes. F. Zhao, X.Z., X.L., characterized the physical and chemical properties of as-prepared samples involving XRD, DRS, FTIR, Raman, FESEM, TEM, AFM, XPS, BET, PL and ESR, assisted by F. Zhang, and Z.L. F. Zhao and X.Z. conducted the electrochemical measurements. F. Zhao and Y.W. performed the theoretical calculations. T.W. and J.G. performed and analysed the photocatalytic results and provided theoretical support. F. Zhao wrote the manuscript with contributions from all authors. All the authors discussed the results.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Y.F. or W.F.

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