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## Hydrogen Terminated Germanene for a Robust Self-Powered Flexible Photoelectrochemical Photodetector

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# Hydrogen Terminated Germanene for a Robust Self-Powered Flexible Photoelectrochemical Photodetector

## Abstract

© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim As a rising star in the family of graphene analogues, germanene shows great potential for electronic and optical device applications due to its unique structure and electronic properties. It is revealed that the hydrogen terminated germanene not only maintains a high carrier mobility similar to that of germanene, but also exhibits strong light–matter interaction with a direct band gap, exhibiting great potential for photoelectronics. In this work, few-layer germanane (GeH) nanosheets with controllable thickness are successfully synthesized by a solution-based exfoliation–centrifugation route. Instead of complicated microfabrication techniques, a robust photoelectrochemical (PEC)-type photodetector, which can be extended to flexible device, is developed by simply using the GeH nanosheet film as an active electrode. The device exhibits an outstanding photocurrent density of  $2.9 \mu\text{A cm}^{-2}$  with zero bias potential, excellent responsivity at around  $22 \mu\text{A W}^{-1}$  under illumination with intensity ranging from 60 to  $140 \text{ mW cm}^{-2}$ , as well as short response time (with rise and decay times,  $t_r = 0.24 \text{ s}$  and  $t_d = 0.74 \text{ s}$ ). This efficient strategy for a constructing GeH-based PEC-type photodetector suggests a path to promising high-performance, self-powered, flexible photodetectors, and it also paves the way to a practical application of germanene.

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# Hydrogen Terminated Germanene for a Robust Self-Powered Flexible Photoelectrochemical Photodetector

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**Abstract:** As a rising star in the family of graphene analogues, germanene shows great potential for electronic and optical device applications due to its unique structure and electronic properties. It was revealed that the hydrogen terminated germanene not only maintains a high carrier mobility similar to that of germanene, but also exhibits strong light–matter interaction with a direct band gap, exhibiting great potential for photo-electronics. In this work, few-layer GeH nanosheets with controllable thickness were successfully synthesised by a solution-based exfoliation-centrifugation route. Instead of complicated microfabrication techniques, a robust photoelectrochemical (PEC)-type photodetector, which can be extended to flexible device, has been developed by simply using the GeH nanosheet film as an active electrode. The device

exhibits an outstanding photocurrent density of  $2.9 \mu\text{A cm}^{-2}$  with zero bias potential, excellent responsivity at around  $22 \mu\text{A W}^{-1}$  under illumination with intensity ranging from  $60 \text{ mW cm}^{-2}$  to  $140 \text{ mW cm}^{-2}$ , as well as short response time (with rise and decay times,  $t_r = 0.24 \text{ s}$  and  $t_d = 0.74 \text{ s}$ ). This efficient strategy for a constructing GeH-based PEC-type photodetector suggests a path to promising high-performance, self-powered, flexible photodetectors, and it also paves the way to a practical application of germanene.

## 1. Introduction

Two-dimensional (2D) materials have recently attracted significant attention in the field of optoelectronic detectors owing to their unique band-structures and various forms of light–matter interaction that benefit from the 2D quantum confinement and tuneable layered-structure. [1–5] Graphene, the most widely explored 2D material and a massless Dirac fermion system, has a promising application in optoelectronic devices owing to its remarkably high carrier mobility and strong interaction with photons over a wide energy range. [6, 7] Due to the absence of a band gap, however, the application of graphene-based photodetectors or phototransistors has been blocked due to its high dark current and low on/off ratio. [8, 9] The recent developed Xenos (X = Si, Ge, Sn, and other group IV-A elements), as both structurally analogous and isoelectronic species to graphene, offer a chance to open up an energy band gap in the electronic band structure, due to their strong spin-orbit coupling and intrinsically buckled structure. [10] Among them, germanene, consisting of germanium atoms with  $sp^2$  and  $sp^3$  hybridization, has received considerable attention due to its unique properties, including tunability of its energy band structure and high carrier mobility as well as a quantum Hall effect. [11–15] These features make germanene a promising material for electronics and optoelectronics, where it exhibits superior potential compared to its bulk counterpart (germanium), which is a typical photoelectric material. In addition, 2D germanene is also a good candidate material for flexible electronics due to its high aspect ratio and ductile nature.

Despite all these advantages, exploration of the application of germanene has suffered due to the challenges to the massive synthesis of high-quality samples. The typical synthesis route is still limited to growing layered germanene on substrates via molecular beam epitaxy (MBE).<sup>[16-20]</sup> On the bright side, the recently successful synthesis of a GeH layered structure has paved a way to the large-scale preparation of hydrogen-terminated germanene by a topochemical deintercalation route. The theoretical and experimental results suggested that the monolayer GeH (germanane) is a direct narrow band-gap semiconductor with high carrier mobility (as high as  $18000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , 5 times higher than that of bulk Ge).<sup>[21, 22]</sup> Consequently, GeH nanosheets are expected to display an extraordinary photo-response performance when they are applied in next-generation photo-electronic devices or even advanced flexible photo-electronics. Nevertheless, the complicated and expensive microfabrication techniques required for constructing GeH nanosheet-based photovoltaic-type or photoconductive-type photodetectors are further impeding the practical application of GeH in photo-electronics, and it is difficult to achieve the adjustment of its photoresponse characteristics.

In this work, solution-processed GeH nanosheets with selected thicknesses have been successfully prepared via a top-down exfoliation of as-synthesised high-quality GeH single crystal. By simply dispersing these nanosheets in solvent as inks for active photoelectrode constructions, an efficient PEC-type photodetector based on 2D hydrogen-terminated germanene can be fabricated without a complicated lithographic process. In addition, benefiting from the facile PEC fabrication process associated with the accessible solution-based GeH nanosheets, flexible GeH photodetectors have been successfully constructed on PEC-based current collectors. With the ability to work in a self-powered mode, the prepared GeH nanosheets in PEC-type photodetectors exhibited a high photocurrent density of  $2.9 \mu\text{A cm}^{-2}$  with zero bias potential, excellent responsivity at around  $22 \mu\text{A W}^{-1}$  under illumination with intensity ranging from  $60 \text{ mW cm}^{-2}$  to  $140 \text{ mW cm}^{-2}$ , and short response time (with rise and decay times,  $t_r = 0.24 \text{ s}$  and  $t_d = 0.74 \text{ s}$ ). Mechanism investigation revealed that the faster

migration of photo-induced holes in thinner GeH nanosheets are the determining factor contributing to the highly-efficient photo-responsivity of GeH ultra-thin nanosheets. The good photo-response capability of the as-prepared flexible device also demonstrated the potential of GeH nanosheets as a key photo-responsive component in self-powered, flexible photo-detectors, which are favourable for future application in portable electronic and optoelectronic devices.

## 2. Result and Discussion

High-quality GeH single crystal was synthesized via a topochemical reaction of  $\text{CaGe}_2$  with hydrochloric acid (HCl) at low temperature (**Figure 1a** and S1 a-c in the Supporting Information (SI)). A powder X-ray diffraction pattern (XRD) of the as-fabricated  $\text{CaGe}_2$  crystal is shown in Figure 1b, which matches well with the hexagonal Zintl phase  $\text{CaGe}_2$  (JCPDS Card NO. 00-013-0299). Taking the  $\text{CaGe}_2$  crystal as a precursor and template, the layered crystalline GeH can be obtained by gently knocking out Ca ions and saturating the surface terminations with H (Figure S2), with the crystal structure confirmed by the XRD pattern shown in Figure 1b. The XRD pattern of GeH single crystal possesses a sole strong diffraction peak and a relatively weak peak, which are indexed to its (002) and (004) facets, matching well with the standard GeH structure (JCPDS Card NO. 01-083-5188). Meanwhile, the Raman spectra (excited by 532 nm laser) shown in Figure S1d confirm the H surface termination in the GeH single-crystal due to the appearance of a peak at around  $226\text{ cm}^{-1}$ , which pure germanium or germanene do not have.<sup>[23-25]</sup> The Raman peaks observed at  $226\text{ cm}^{-1}$  and  $303\text{ cm}^{-1}$  correspond to the  $A_{1g}$  (out-of-plane) and  $E_{2g}$  (in-plane) mode of hexagonal GeH single crystal, which is in strong agreement with the reported investigations.<sup>[20, 21]</sup> The optical images of bulk GeH single crystal (Figure S3a-b) show a metallic lustrous surface with a layered structure, which is further proved by the scanning electron microscopy (SEM) images. As displayed in Figure S3c, the low-magnification SEM image that there is a clearly graphite-like structure for stackable GeH, and the high magnification SEM image in Figure S3d presents a sharply defined edge of GeH single crystal in detail. In order to present a large surface area and facilitate the construction of

electrodes, sonication was applied to exfoliate the layered GeH single crystal into nanosheets. As shown in Figure 1b, all the diffraction peaks are readily assigned to the hexagonal GeH phase, indicating the random arrangement of nanosheets during sonication. The SEM image (Figure S3e) of few-layer sample of exfoliated GeH on the Si/SiO<sub>2</sub> substrate was collected, with the typical feature of a relatively large lateral area ( $\sim 30 \times 20 \mu\text{m}$ ). Moreover, the optical properties of the layered GeH nanosheets were investigated by ultraviolet-visible (UV-Vis) spectroscopy, as displayed in Figure S1e, showing that strong absorption occurs in the visible spectral region. The Tauc plot method was utilized to estimate the optical band gap, with the linear region of the plot of  $(\alpha hv)$  versus photon energy  $(hv)$  extended ( $\alpha$ : absorption coefficient;  $h$ : Planck's constant;  $v$ : light frequency).<sup>[26]</sup> The analysed band gap of GeH single crystal is  $\sim 1.66$  eV (inset image of Figure S1e), indicating an appealing candidate for a visible-light harvesting photoelectronic device. In addition, the thickness-dependent band gap of GeH nanosheets creates the opportunity to regulate its optical properties with a further impact on their photodetector performance. The X-ray photoelectron spectroscopy (XPS) spectrum in Figure S1f reveals that the two peaks centred at binding energy of 1217.7 eV and 1248.8 eV can be attributed to the Ge 2p<sub>3/2</sub> and Ge 2p<sub>1/2</sub> in GeH, respectively. The presence of GeO<sub>2</sub> peaks is derived from the partial oxidation on the surfaces of GeH nanosheets. GeH nanosheets with controllable average thickness can be obtained *via* centrifuging the exfoliated GeH nanosheets at different speeds, providing a platform for investigation of the thickness dependence of the optical properties of GeH nanosheets. The different heights of GeH nanosheets centrifuged at 500 rpm, 1000 rpm, 1500 rpm, and 2000 rpm were evaluated with atomic force microscopy (AFM), and the corresponding height distribution histograms were also analysed with Gaussian fittings, as shown in Figure 1c, respectively. A decrease in the average thickness of exfoliated nanosheets was successfully achieved by increasing the centrifugation speed, from  $\sim 170$  nm (500 rpm) to 1.54 nm (2000 rpm). It should be noted that the thinnest height of the GeH nanosheets is about 0.6 nm, which is consistent with 5.5 Å of GeH monolayer along the [001]

direction, indicating the successful synthesis of GeH monolayers. The optical image of a GeH dispersion centrifuged at 1500 rpm with the Tyndall effect is shown in Figure 1d, which demonstrates the homogeneous nature of the dispersion. This is further confirmed by the AFM images showing a uniform distribution of GeH flakes, and their corresponding thickness with a typical height of 2.94 nm, as displayed in Figure 1d. Moreover, transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were also employed to investigate the crystal structure and the composition of exfoliated GeH nanosheets (1500 rpm). The TEM image of ultrathin GeH nanosheets displayed in Figure 1e reveals the typical hierarchical nanosheet morphology, and the corresponding SAED pattern (inset of Figure 1e) clearly demonstrates that the highly-crystalline nanosheets have a hexagonal structure with a [001] crystalline orientation. In addition, the elemental mapping image in Figure S3f demonstrates the homogenous spatial distribution of Ge element in the as-prepared whole nanosheets.

The successful synthesis of GeH nanosheets with controllable thickness *via* a chemical route offer a great advantage for the application of germanene-related 2D materials, especially for constructing electrodes. Taking an electrode fabricated from a paste containing GeH nanosheets with an average thickness of about 2.94 nm (1500 rpm) as a typical sample, the photoresponse performance of GeH-nanosheet (NS) based photo-electrode was evaluated by systemic photoelectrochemical measurements under simulated sunlight irradiation. Since the photoresponse of the GeH photodetector was not stable in acidic solution (0.5 M H<sub>2</sub>SO<sub>4</sub>) or alkaline solution (0.5 M KOH), as demonstrated in Figure S4a-b, neutral solution (0.5 M Na<sub>2</sub>SO<sub>4</sub>) was utilized as the electrolyte for the whole measurement system. Figure S5a presents the current density of the GeH photoelectrode under light and in the dark in the neutral 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte via linear sweep voltammetry (LSV) curves. The GeH working electrode exhibits an anode photocurrent, showing the steady rising trend of photocurrent density from -0.5 V to 1.0 V. The relationship between photocurrent density and bias potential was measured



under light irradiation, as shown in **Figure 2a**. The photocurrent density obtained from the as-fabricated GeH electrode increased from  $2.9 \mu\text{A cm}^{-2}$  to  $10.9 \mu\text{A cm}^{-2}$  when the bias voltage changed from 0 V to 1 V, indicating a bias potential-dependent response of the photocurrent. Such a relationship is reasonable according to the reported studies, since the external potential could effectively cause electron-hole acceleration, and separation as well as transportation, resulting in a higher photocurrent in the circuit.<sup>[27]</sup> Moreover, it should be noted that the GeH based PEC detector had a remarkable photoresponse to the simulated sunlight irradiation without any external bias potential, revealing the possibility of a GeH photodetector as self-powered device. In order to measure the cycling stability of the GeH photodetector under different bias potential from 0 V to 1 V, the incident light was alternatively switched on and off with the power intensity of  $100 \text{ mW cm}^{-2}$  (Figure S5b). The photodetector shows highly repeatable switched behaviour between the “on” and “off” states with a time interval of 10 s. In addition, the rise time and decay time were deduced from one cycle of photoresponse presented in Figure 2b under 0 V bias potential, in order to quantitatively evaluate the response speed of the GeH photodetector. The  $t_r$  ( $t_d$ ) is defined to describe the time interval for the response rising (falling) from 10% (90%) to 90% (10%), which were calculated as 0.24 s and 0.74 s using the formula

$$I = I_0 - A \exp(-t/\tau) \quad (1)$$

( $A$ : scaling constant;  $\tau$ : relaxation time constant), respectively.<sup>[28, 29]</sup> The response and recovery time of the GeH photodetector is relatively competitive when compared with other PEC-type photodetectors. (See the statistical data in Table S1.)

In addition to the bias potential, the intensity and wavelength of incident light also have a considerable impact on the photoresponse of the PEC system, which are worth investigation. Figure 2c plots the photocurrent density of the GeH detector under different power densities ranging from  $60 \text{ mW cm}^{-2}$  to  $140 \text{ mW cm}^{-2}$  at 0 V. It is clearly observed that the photoresponse is rising from  $1.39 \mu\text{A cm}^{-2}$  to  $3.29 \mu\text{A cm}^{-2}$  under forward light intensity. Further exploration

of the photoresponse characteristic in Figure 2d, it describes the quantitative relationship between the photocurrent density and the power intensity that is extracted from Figure 2c. The photocurrent density exhibits a relatively good linear relationship with the light intensity, indicating the high crystallinity of GeH nanosheets with relatively few traps or defects. Furthermore, to evaluate the sensing performance of the photocurrent as a function of the light intensity, the responsivity ( $R$ ), described as the photocurrent generated per unit power of the incident light on the effective area, is introduced. The  $R$  is obtained using the formula:

$$R = (I_{light} - I_{dark})/PS \quad (2)$$

where  $I_{light}$  is the current under light illumination,  $I_{dark}$  is the dark current,  $P$  is the light illumination intensity, and  $S$  refers to the effective illuminated area. The calculated responsivity under different incident light intensities is presented in Figure 2d. As illustrated in the figure, the GeH based photodetector shows a higher photoresponsivity in comparison to other PEC-type photodetectors, [30, 31] with around 22–24  $\mu\text{A W}^{-1}$  in the range from 60  $\text{mW cm}^{-2}$  to 140  $\text{mW cm}^{-2}$ . Besides, the specific detectivity ( $D^*$ ), an index to evaluate the smallest detectable signal is also calculated to evaluate the performance of the detector. It could be described according to the following equation:

$$D^* = (RS^{\frac{1}{2}})/(2eI_{dark})^{1/2} \quad (3)$$

where  $R$  is the responsivity,  $A$  is the effective area of the photodetectors ( $S=2 \text{ cm}^2$ ),  $e$  is the electronic charge ( $1.6 \times 10^{-19} \text{ C}$ ), and  $I_{dark}$  is the dark current. Based on the above equation as well as the experimental data ( $I_{dark} = 0.74 \times 10^{-6} \text{ A}$ ,  $R = 2.305 \times 10^{-5} \text{ A}$ ), the  $D^*$  of the GeH based PEC photodetector is calculated to be  $6.70 \times 10^7 \text{ Jones}$  with the power intensity of  $100 \text{ mW cm}^{-2}$  under 0 V bias potential. Figure 2e displays the photocurrent density of the GeH detector at an illumination intensity of  $20 \text{ mW cm}^{-2}$  over the different illumination wavelengths of 365 nm, 436 nm, 546 nm, 630 nm, and 730 nm. The photocurrent density increases from  $3.93 \mu\text{A cm}^{-2}$

to  $6.38 \mu\text{A cm}^{-2}$  as the wavelength increases from 365 nm to 630 nm, and it starts to decrease to  $2.58 \mu\text{A cm}^{-2}$  when the wavelength is over 630 nm. In addition, the dependence of the wavelength on the photoresponsivity of the PEC-type detector shows a similar trend of that of the absorption. The critical peak of the responsivity is at the wavelength of about 600 nm, strongly corresponding to the maximum absorption peak at about 600 nm in the UV-Vis spectra. This kind of photoactivity is practically related to the working mechanism of the optoelectronic device.<sup>[32, 33]</sup> Under visible-light illumination, the photoenergy at 730 nm is sufficient to lift the electrons directly from the valence band to the conduction band in the GeH nanosheets, resulting in a rising photoresponsivity. It should be noted that a higher energy photon does not lead to a consistent high photoresponse, which may be due to the improved absorption of photons and reduced lifetime of the electron-hole pairs at or near the surface of the GeH nanosheets.<sup>[34]</sup> We engaged in further exploration of the cycling stability of the GeH photodetector with switch “on” and “off” behaviour, since the performance of the PEC-type detector strongly hinges on the stability of the as-prepared GeH electrode. As shown in Figure S6, the photoresponse test was performed on GeH photodetector placed in 0.5 M  $\text{Na}_2\text{SO}_4$  for 1 hour, 1 day and 1 week, respectively. It can be clearly observed that the photodetector still maintains good on/off characteristics after being placed for one week, which indicates that the GeH photodetector has extraordinary environmental stability. In addition to the cycling stability, the thermal stability of the GeH photodetector are also investigated, through acquiring the photocurrent at different temperatures ranging from room temperature ( $\sim 21 \text{ }^\circ\text{C}$ ) to  $80 \text{ }^\circ\text{C}$  (Figure S7a). As shown in Figure S7a, it is clearly observed that the response photocurrents at  $21 \text{ }^\circ\text{C}$ ,  $40 \text{ }^\circ\text{C}$ ,  $60 \text{ }^\circ\text{C}$ , and  $80 \text{ }^\circ\text{C}$  are nearly the same, indicating good thermal stability of this GeH based PEC electrode. The relationship between the photocurrent and testing temperature has been further plotted in figure S7b. Furthermore, an *in-situ* temperature-dependent XRD experiment was also conducted to further clarify the structural stability of GeH. As shown in Figure S7c, no obvious change was found in XRD pattern from room temperature to  $100 \text{ }^\circ\text{C}$ , indicating the good stability of GeH

until the temperature increases to 100 °C. Based on the aforementioned results, the remarkable photocurrent density, faster rise (decay) time, and outstanding responsivity of GeH nanosheet guarantee outstanding advantages for application in visible-light photodetectors.

Based on the tunability of the electronic structure of germanene, the photoresponsive properties of GeH nanosheets are able to be tuned by controlling the thickness of the GeH nanosheets. Four different kinds of GeH nanosheets with an average height of 167.3 nm (500 rpm), 22.8 nm (1000 rpm), 2.94 nm (1500 rpm), and 1.54 nm (2000 rpm) were used to construct working electrodes, and the corresponding performances were evaluated under simulated sunlight irradiation, as shown in **Figure 3a**. It can be found that there is a significant rise in the photocurrent density with decreasing thickness. Such extraordinary photoactivity of the thickness-dependent GeH nanosheets could be ascribed to their intrinsic optical and electrical properties. In order to evaluate the capability of charge separation and diffusion of four kinds of GeH based photodetectors, the current rise and decay curves (Figure S8a-b) deduced from the aforementioned four kinds of photoresponse cycles are fitted *via*  $I = I_0 - A \exp(-t/\tau_r)$  and  $I = I_0 - A \exp(-t/\tau_{d1}) - B \exp(-t/\tau_{d2})$ . In the formulas,  $\tau_r$ ,  $\tau_{d1}$ , and  $\tau_{d2}$  are the time constants for the rise edges, the fast-response components for decay edges, and the slow-response components for decay edges, respectively. The fast-response component ( $\tau_{d1}$ ) results from the photoexcited electron-hole recombination, and the slow-response component ( $\tau_{d2}$ ) is associated with the existing trap states that slow down the recovery time by preventing carrier recombination.<sup>[35-37]</sup> As the fitting data showed in Figure 3b, both the  $\tau_r$  and the  $\tau_d$  exhibited a shorter trend when the centrifugation of GeH increased from 500 rpm to 2000 rpm. The results indicate that GeH nanosheets with 2000 rpm centrifugation possess the the fastest response speed, which means the charge separate promptly and achieve rapid carrier transport in photodetectors. This is due to the quantum confinement effect of the two-dimensional size. In detail, the reduction in the thickness of GeH nanosheets applied in the PEC electrode, offers a shorter carrier transport path, thus accelerating the migration of yielding photo-electron or hole

to the surface. In addition, the ultrathin thickness allows carriers to be confined to a single or several atomic layers, thereby reducing cross-layer cross-transport during carrier transfer.<sup>[38, 39]</sup> The intrinsic fast carrier mobility of 2D GeH also facilitates the separation of photogenerated electron-hole pairs. Therefore, the fast separation and diffusion process of electron-hole pairs guarantees the rapid photo-response of GeH nanosheets reduced from three dimensions to two dimensions. Under light irradiation, by competition with the recombination of these photo-generated electrons and holes, a stable photocurrent is obtained when the amount of photo-induced electrons and the transferred electrons reach equilibrium. After the light is removed, photo-generated electrons and holes cease to be generated in GeH, and the photocurrent drops sharply. However, due to the hysteresis effect of the current, a small part of the retained photo-induced carriers are still transferring, which may cause the decay time of the photocurrent curve to be longer than the rising time. More obvious hysteresis effects are normally found in the electrodes which possessing higher photo-induced current change, which then results in longer decay time. As shown in Figure 3b, the GeH nanosheets electrode obtained at 1500 rpm has a larger decay time than that of the samples obtained at 500 rpm and 1000 rpm, due higher photocurrent was obtained with the 1500 rpm sample with thinner GeH nanosheets. It should be noted that the decay time for the 2000 rpm sample, the thinnest GeH nanosheets sample, is lower than others. The reason might be that the amount of retained photo-induced carriers in the 2000 rpm sample is much smaller, due to its ultra-small lateral dimension as well as the small volume (as shown in Figure S9). In addition to the charge separation and diffusion, light absorption and charge transfer at the electrode/electrolyte interface are the other two major processes that take place in PEC-type detector.<sup>[40]</sup> Generally, the light absorption capability is regarded as an important parameter to determine the efficiency of sunlight utilization, and it further affects the performance of a photodetector. The optical properties of the centrifuged GeH nanosheets were investigated by UV-Vis spectra, and the Tauc plot method was utilized to estimate the optical band gap, as displayed in Figure 3c and S8c. The resultant band gaps of

1.69 eV, 1.75 eV, 1.78 eV, and 1.82 eV belong to the precipitated GeH with 500 rpm, 1000 rpm, 1500 rpm, and 2000 rpm centrifugation, respectively, implying a trend towards increasing band gap energy with reduced thickness. For the materials with large band gap, a photon with higher energy (usually UV light) is required to promote an electron from the valence band to the conduction band, indicating the inefficient harvesting of visible light. Although the thinner GeH nanosheets are inferior in terms of visible light harvesting, the synergistic effects of the above-mentioned three components contribute to the outstanding photocurrent of the photodetector with thin GeH nanosheets compared with those that have the thick ones. As for the aspect of charge transfer at the interfacial surface, the electrodes fabricated with the thinnest nanosheets acquire more intimate contact with the indium tin oxide (ITO) substrate and a higher interfacial contact area with the electrolyte due to the huge surface area of the thinnest GeH with 2000 rpm centrifugation.<sup>[41]</sup> This could further promote fast charge transfer through the external circuit, as confirmed by the much lower interfacial charge-transfer resistance derived from the electrochemical impedance spectroscopy (EIS) curves in Figure 3d. Obviously, the charge separation and diffusion as well as the charge transportation play crucial roles in the synergistic effects, thus leading to the highest photocurrent density of the thinnest GeH based photodetector. Adjusting the thickness of the GeH nanosheets would give rise to changes in the response time as well as the interfacial resistance, so that we could modulate the photoresponse of the PEC-type detector.

To more deeply reveal the electronic properties of GeH nanosheets, the theoretical calculations of the electronic structure via the Vienna ab initio Simulation Package (VASP) were conducted.<sup>[42-45]</sup> **Figure 4a** and S10a-e show the electronic band-structures for monolayer, bilayer, four-layer, six-layer, eight-layer, and bulk GeH, and the calculated band gaps of few-layer GeH nanosheets are summarized in orange square curve of Figure 4b with 1.79 eV, 1.73 eV, 1.68 eV, 1.66 eV, 1.66 eV, and 1.65 eV, respectively, indicating a reducing trend in the band gap with increasing layers. The trend in the calculated results with GeH thickness is in

agreement with that in the experiments, and the corresponding values are similar to the experimental energy gaps. The increasing thickness would enhance the interlayer interaction of GeH nanosheets, lead to the larger dispersion of the valence bands (conduction bands), and finally result in a smaller band gap. The band gap would have an impact on the optical lighting harvesting, while the effective mass would affect the carrier mobility and further alter the transport properties of the GeH based PEC-type detector. The carrier mobility is inversely proportional to the effective mass according to the formula:

$$\mu = q\tau/m^* \quad (4)$$

( $\mu$ : carrier mobility,  $q$ : charge,  $\tau$ : scattering time of a charge carrier,  $m^*$ : effective mass), and the effective mass is defined as

$$m^* = \hbar^2 / (4\pi^2 (\partial^2 E / \partial k^2)) \quad (5)$$

( $\hbar$ : Boltzmann constant,  $E$ : dispersion relation for the calculated band,  $k$ : the reciprocal lattice vector). The calculated effective masses of GeH with different layers for electrons (holes) at the conduction band minimum (valence band maximum) are presented in Figure 4b. As can be seen, the effective masses for holes (green stars curve in Figure 4b) become slightly larger with increasing layers of GeH nanosheets, and the values for electrons (green spherical curve) are nearly the same, which results in larger effective masses for electrons as well as holes and reasonable, but slower transportation of carriers. Therefore, the decreasing effective masses of the thinner GeH nanosheets could improve the carrier transportation and thus enhance the photocurrent of the PEC-type detector.

More importantly, the GeH nanosheets could further be utilized in a flexible photodetector based on bendable substrates with excellent mechanical flexibility and durability, indicating that GeH nanosheets are promising candidate for smart and wearable optoelectronics. The fabrication of a GeH nanosheet film through a repeated spin-coating process on an ITO substrate is schematically described in **Figure 5a**, and the optical image of the successfully fabricated composite film is shown in Figure 5b, which presents excellent flexibility and

transparency. In order to achieve a flexible photodetection system, poly (ethylene terephthalate) (PET) coated with platinum was used as the bottom electrode, which was integrated with the aforementioned GeH composite film (Figure 5c). The flexibility of the photodetectors was investigated with respect to different bending angles ( $0^\circ$ ,  $82^\circ$ , and  $143^\circ$ ) under periodic simulated sunlight at the bias potential of 0 V, while the corresponding photoresponse activity is presented in Figure 5d-f, respectively. The devices presented steady cycles of photocurrent density when bending from  $0^\circ$  to  $143^\circ$ , indicating the good mechanical stability of the self-powered photodetector. The obtained results illustrated the mechanical flexibility and electrical stability of the flexible photodetector, paving the way for the construction of GeH-based, self-powered and flexible photodetectors.

### 3. Conclusion

In summary, GeH single crystal was successfully synthesized on a large scale via topochemical deintercalation, with a direct band gap at around 1.66 eV. They were thus first applied in a visible light PEC-type detector, and offered an outstanding platform to achieve effective sensing performance. The high quality of the crystalline GeH nanosheets with a highly [001] preferred orientation was identified by XRD and SAED, in which sharp diffraction peaks of their (002) and (004) facets, and clear hexagonal diffraction patterns could be observed, respectively. When using the exfoliated GeH nanosheets as photoanode of PEC-type photodetector, it exhibited excellent photocurrent density and outstanding responsivity as well as a short response time, compared with other PEC-type photodetectors tested under the same experimental conditions. Moreover, GeH nanosheets with a diverse thickness distribution were obtained through the centrifugation method, and the thickness-dependent photoresponse performance of GeH nanosheets was investigated. The performance of the PEC detector could be efficiently tuned via the thickness of the GeH nanosheets, due to the different synergistic effects of efficient visible light harvesting, fast electron-hole separation, and improved



interfacial charge transfer. Furthermore, the GeH based flexible photodetector showed outstanding flexibility and stability at 0 V bias, laying the foundation for a further wearable application system. This work opens a new avenue to GeH nanosheet based PEC-type detectors, and thus contributes to promising investigations and applications for GeH based Xene nanomaterials as photoelectrodes.

#### 4. Experimental Section

*Synthesis of GeH single crystal/nanosheets:* Commercially available Ge powder and Ca chips were purchased by Sigma-Aldrich (AR grade) and used as received without further purification. Zintl phase  $\text{CaGe}_2$  was prepared through high temperature calcination in a muffle furnace. Briefly, a certain amount of Ge and Ca were sealed in a quartz tube, which was evacuated, and then heated at a high temperature (1010 °C). Bulk  $\text{CaGe}_2$  was obtained after cooling down to the room temperature. After immersing the  $\text{CaGe}_2$  in concentrated hydrochloric acid at -30 °C and stirring for 8 days, the GeH single crystals were finally obtained after washing and separated using ethanol and methanol.

To exfoliate the GeH, the as-prepared GeH single crystal was dispersed in ethanol solution and ultrasonicated using a sonic tip probe at the room temperature. Following sonication, the obtained homogeneous liquid was centrifuged at different speeds (500 rpm, 1000 rpm, 1500 rpm, 2000 rpm) for 20 min to obtain GeH nanosheets with different thicknesses.

*Characterization:* XRD was conducted on the fabricated (GBC MMA diffractometer) with  $\text{Cu K}\alpha$  radiation at a scanning rate of  $1.5^\circ \text{ min}^{-1}$ . The morphologies and crystal structures were investigated by field emission scanning electron microscopy (JSM-7500FA, JEOL), and transmission electron microscopy (JEM-2011F, JEOL, 200 kV). Optical images were collected with a Leica DM6000 microscope. Atomic force microscopy (MPF-3D, Asylum Research) was utilized to measure the thickness of the centrifuged nanosheets. Ultraviolet-visible absorption

spectra were acquired on a Shimadzu UV-3600. Raman spectra for the specific mode was detected via a Nanofinder system. XPS was carried out on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer with monochromatic Al K $\alpha$  radiation under vacuum at  $2 \times 10^{-6}$  Pa.

*Working electrode preparation and PEC measurements:* A certain amount of exfoliated nanosheets (1 mg) was dispersed in 1 ml ethanol solution to form a homogeneous dispersion. Then, indium-tin oxide (ITO, 20 mm  $\times$  10 mm  $\times$  10 mm) conductor glass was applied as the substrate for the working electrode, and the aforementioned solution was uniformly coated thereon. After drying under ambient conditions all night, spatially uniform photosensitive material having a loading of around 0.5 mg cm $^{-2}$  was obtained on the substrate.

PEC testing was performed in a conventional three-electrode system with 0.5 M Na $_2$ SO $_4$  (pH = 6.6) electrolyte, with the setup consisting of a working electrode (GeH nanosheets coated on ITO), a counter electrode (platinum flake), and a reference electrode (saturated calomel electrode). The photoresponse activity was evaluated on an electrochemistry workstation (CH Instruments, Inc. Shanghai) at a scan rate of 10 mV s $^{-1}$  under irradiation by a 350 W xenon arc lamp (CHF-XM 350). The xenon lamp was used as the source for simulated sunlight, and its illumination intensity was fixed at 100 mW/cm $^{-2}$  unless declared otherwise.

*Computational methods:* A density functional theory (DFT) computational study of the electronic structures was performed using the Vienna *ab initio* Simulation Package (VASP). VASP implements the DFT in the Kohn–Sham formulation using a plane wave basis and projector-augmented wave formalism (PAW).<sup>[46, 47]</sup> Since the Perdew-Burke-Ernzerhof (PBE) functional underestimates the band gap, the hybrid functional method (HSE06)<sup>[48]</sup> was used to calculate the electronic structures of the few-layer GeH. A 25% ratio of nonlocal Fock exchange was set in the HSE06 calculation. Ge 4s4p and H 1s electrons were treated as the valence electrons in the PAW potentials. The energy cut-off of the plane wave basis set was 500 eV, and the atomic force convergence accuracy at each atomic site was set to be 10 $^{-4}$  eV/Å. In the band structure calculations, one hundred k-points were set along the high symmetry points K

and G, and also G to M. The effective masses of few-layer GeH were simulated by seven points around the G point in the Brillouin zone. Our effective mass for monolayer GeH matched well with the reference data,  $0.09 m_0$  for electrons and  $0.43 m_0$  for holes. <sup>[21]</sup> Specific details can be seen in the Supporting Information.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

2D materials, germanene, GeH, PEC photodetector, self-powered

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**Figure 1.** (a) Process of GeH synthesis. (b) XRD pattern of  $\text{CaGe}_2$ , GeH nanosheets (GeH-NS), and GeH single crystal (GeH-SC). Insets: optical images of  $\text{CaGe}_2$ , GeH-NS, and GeH-SC. (c) Height distribution histograms for GeH nanosheets centrifuged at 500 rpm, 1000 rpm, 1500 rpm, and 2000 rpm. (d) Optical image, AFM image, and its corresponding height profiles for GeH nanosheets centrifuged at 1500 rpm. (e) TEM image of GeH nanosheets. Inset: corresponding SAED.

**Figure 2.** (a) Photocurrent density of GeH photodetector under external potential from 0 to 1.0 V in 0.5 M  $\text{Na}_2\text{SO}_4$ . Inset: Schematic representation of GeH based PEC photodetector. (b) Rise time ( $t_r$ ) and decay time ( $t_d$ ) of photocurrent density ( $I_p$ ). (c) Photocurrent density of GeH photodetector under different power intensities (60, 80, 100, 120 and 140  $\text{mW cm}^{-2}$ ) at 0 V. (d)

Photocurrent density and responsivity as functions of the power intensity at 0 V. (e) UV-Vis absorption spectrum and photocurrent density of the GeH photodetector in 0.5 M Na<sub>2</sub>SO<sub>4</sub> under different light wavelengths (365, 436, 546, 630, 670, and 730 nm) at 0 V.

**Figure 3.** (a) Photocurrent density of GeH nanosheets centrifuged at various speeds (500 rpm, 1000 rpm, 1500 rpm, and 2000 rpm) under simulated light irradiation. (b) Average rise time and decay time of four kinds of GeH photodetector. (c) UV-Vis absorption spectra of four kinds of GeH nanosheets. (d) EIS plots and fitting curves of four kinds of GeH nanosheets. Inset: Randles equivalent circuit. ( $Z'$ : real part of the impedance;  $Z''$ : imaginary part of the impedance.)

**Figure 4.** (a) Electronic band structure of bulk GeH. (b) Comparison of the band gap values (Orange square curve), electron effective mass (Green spherical curve) and hole effective mass (Green stars curve) for 1L, 2L, 4L, 6L, 8L, and bulk GeH, where L = monolayer. Inset: The differential charge density of GeH monolayer, and the charge density is set to 0.008e. Yellow: charge accumulation region; blue: charge depletion region.



**Figure 5.** (a) Schematic illustration of spin-coating GeH nanosheets on ITO substrate. (b) Optical image of the bendable device made from GeH nanosheets on the ITO substrate. (c) Schematic representation of the flexible GeH photodetector in a flexed state. *I-t* curves of the flexible GeH photodetector bent to different degrees of (a) 0°, (b) 82°, and (c) 143° under a bias potential of 0 V under simulated sunlight.