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GeH: A Novel Material as Visible-light Driven Photocatalyst for Hydrogen Evolution†

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A novel 2D material germanane (GeH), which was synthesized by ion-exchange approach, was firstly found to have photocatalytic performace in hydrogen evolution of water splitting and decomposition of organic contaminants under illumination of visible light (λ≥420nm).

With unique 2D structures, graphene-like materials including transition metal chalcogendes (e.g. MoS_2, WS_2), transition metal oxides (e.g. V_2O_5) and others have attracted more attention in recent years.[1,2] Comparing to graphene, graphene-like materials are also formed by van der Waals interaction, which enables stacking of the atomic layers,[3] but there are great differences in structures and electronic properties between the two. Different from graphene, which need to be activated by doping or modifications, graphene-like materials can be directly utilized as catalysts without any modification, e.g. MoS_2 has been reported to have high activity as catalysts in electrochemical hydrogen evolution.[4,5] In recent years, graphene-like materials have been reported to be of great applicable value in photocatalysis. MoS_2 nanosheet coated TiO_2 nanobelts showed a high photocatalytic hydrogen evolution even without Pt as cocatalyts.[6] Nanoclusters of MoS_2 and WS_2 combined with TiO_2 contributed to the transfer of photo-generated electrons from TiO_2 particles, resulting in high efficiency in photo-oxidization of organic contaminants, i.e., methylene blue and 4-chlorophenol.[7] The novel graphene-like $g-C_3N_4$ exhibited high activity in hydrogen evolution of water splitting and decomposition of organic pollutions under irradiation of visible light.[8]

Recently, Goldberger et al.[9] reported a novel graphane-like GeH, which has single-atom layers stacked 2D structure. And its electron mobility is reported to be five time higher than that of bulk germanium[10] and ten times higher than silicon, which indicates that GeH has a promising application in photocatlysis. The properties of GeH sheets were studied by density-functional theory (DFT) calculations and probed their dependence on applied uni-axial compression.[11] Due to the quantum confinement, many-body effects play a pivotal role in quasi-particle excitations and optical absorption spectra, which leads to strongly bound excitons in GeH with considerable binding energies.[12] And the study of the electronic properties of GeH as photosensitizers on the anatase TiO_2 (101) surface has achieved great progress by hybrid density functional calculations.[13] But until now, there are no relevant reports of photocatalytic experimental properties of GeH.

Herein, GeH, which was synthesized by using ion-exchange method, was found for the first time to exhibit photocatalytic activities in hydrogen evolution of water splitting and decomposition of organic contaminants. The electronic and band structure of GeH were investigated by the x-ray photoelectron spectroscopy (XPS) and electronic density of states (DOS) calculation. A possible mechanism was proposed to illustrate the photocatalytic process.

In a typical synthetic procedure, $CaGe_2$ crystals were used as precursor, which were prepared by the co-solvent process using Pb as a reactive flux, and then $CaGe_2$ reacted with concentrated HCl following an ion-exchange process, which can be described in the following chemical equation:

$$CaGe_2 + HCl \rightarrow GeH + CaCl_2$$
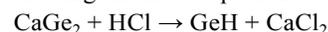
GeH was obtained by the substitute of Ca by H in $CaGe_2$ (more detailed experiments to see ESI†). Fig. 1a and b show the X-ray powder diffraction (XRD) patterns of $CaGe_2$ and GeH, respectively. Most XRD peaks of as-prepared $CaGe_2$ are consistent with those of the standard $CaGe_2$ samples (from JCPDS No.13-299), other peaks are belong to excessive Pb solvent, indicating that the as-prepared samples are $CaGe_2$ with little Pb as impurity.

After the ion-exchange process, XRD peaks of samples are changed and consistent with the peaks of GeH as previous reports,[9] and no peaks of Pb can be observed in XRD patterns,
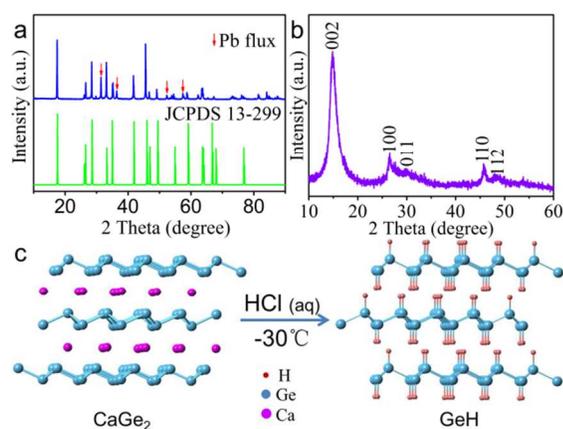
Fig. 1 a) XRD patterns of the as-prepared CaGe₂ and standard CaGe₂ taken from JCPDS file (no. 13-299). b) XRD patterns of the as-prepared GeH. c) Schematic illustration of crystal structures transition of CaGe₂ in concentrated HCl to GeH at low temperatures. (Calcium = magenta, Germanium = light blue, Hydrogen = red).

implying that obtained samples are GeH with high purity and Pb is dissolved in concentrated HCl solution. The crystal structural transformations from CaGe₂ to GeH are illustrated as shown in Fig. 1c. Compared to the original CaGe₂ unit cell parameters of a = 3.987 Å, c = 30.0582 Å, the Ca^{2+} in CaGe₂ was replaced by the H atoms resulting formation of GeH which belonged to 2H unit cell with a= 3.880 Å and c= 11.04 Å (5.5 Å per layer). During the reaction, the powders become reddish brown and lose the initial metallic luster of CaGe₂.[14] As shown in scanning electron microscopy (SEM) images (Fig. 2a), the morphologies of as-prepared GeH has graphite-like structure stacked by layers of GeH. From the high-resolution transmission electron microscopy (HRTEM) image (Fig. 2b), the spacing between the adjacent fringes was measured to be ca. 0.259 nm, which match well with the (112) plane spacing of hexagonal GeH. The UV-Vis-NIR diffused reflectance spectrum shown in Fig. 2c indicates the as-prepared GeH has a strong light absorption in the whole visible light region. The band gap is 1.58 eV according to the $(\alpha h v)^{1/2}$ vs (hv) curve of GeH shown in the inset of Fig. 2c.
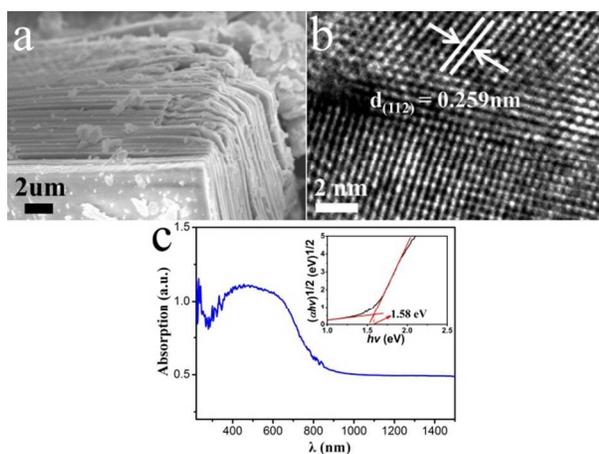

Fig. 2 a) and b) are SEM and HRTEM images of GeH, respectively. c) is UV-Vis-NIR diffuse reflectance spectrum of GeH. The inset shows the $(\alpha h v)^{1/2}$ vs (hv) curve of GeH.
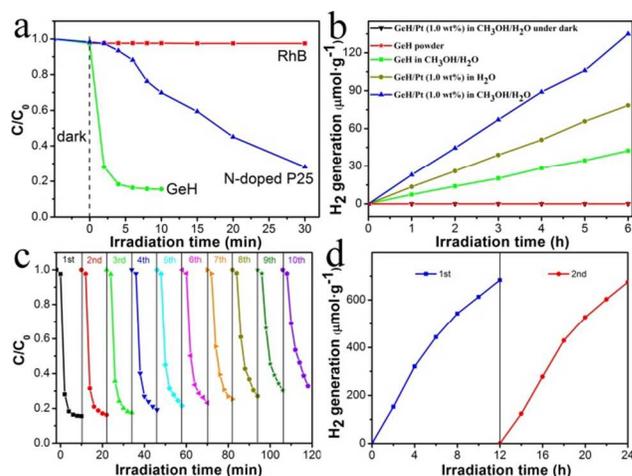

Fig. 3 a) Photocatalytic degradation of RhB over GeH and N-doped P25 under irradiation of visible light (λ≥420 nm).b) Photocatalytic H₂ evolution of GeH in different conditions: GeH/Pt (1.0 wt%) in H₂O/CH₃OH (blue), GeH/Pt (1.0 wt%) in H₂O (yellow), GeH in H₂O/CH₃OH (green), GeH/1.0 wt% Pt in H₂O/CH₃OH under dark (black) and GeH powder only (red) under visible-light (λ≥420 nm) irradiation. c) and d) Irradiation–time dependence of the relative concentration C/C₀ of the RhB dye and the amount of H₂ evolution in solution over GeH during cycling photocatalytic experiments under visible light.

The photocatalytic activity of GeH was estimated by the degradation of Rhodamine B (RhB) under visible light (λ≥420nm) irradiation. As shown in Fig. 3a, GeH has a higher photocatalytic activity than that of N-doped P25. 82% RhB is decomposed over GeH in 4 minutes, while only 70% for N-doped P25 in 30 minutes. Assuming that the photodegradation procedure belongs to pseudo-first-order reaction, RhB degradation rate over GeH (0.197 min⁻¹) is about six times faster than N-doped P25 (0.0325 min⁻¹). No RhB is decomposed when the reaction is carried under dark, which excludes the adsorption of RhB in photocatalytic degradation.

The hydrogen evolution of water splitting by photocatalysis is significant for utilization of solar energy. The photocatalytic hydrogen evolution of GeH was also investigated as shown in Fig. 3b. Hydrogen evolution reactions were carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system.[15,16] In a typical photocatalytic hydrogen experiment, 50 mg of catalyst was homogeneously dispersed in 100 ml aqueous solution containing 30 % methanol in volume (see details in the ESI†). The amount of generated hydrogen is measured by the GC (N₂ as carrier gas) equipped with a TCD detector. As shown in Fig. 3b, when GeH was loaded Pt (GeH/Pt (1.0 wt %)) and the CH₃OH was used as hole scavenger, GeH/Pt (1.0 wt %) exhibits high activity in hydrogen evolution under irradiation of visible light (λ≥420 nm) and the generation rate is about 22 μmol•h⁻¹•g⁻¹. The generation rate of H₂ is about 13 and 7μmol•h⁻¹•g⁻¹ for GeH/Pt (1.0 wt %) in H₂O and GeH in H₂O/CH₃OH, respectively (Fig. 3b). The rate of GeH/Pt (1.0 wt %) in H₂O/CH₃OH is 1.8 and 3 times faster than that of GeH/Pt (1.0 wt %) in H₂O and GeH in H₂O/CH₃OH, respectively. To exclude the generation of H₂ from the decomposition of GeH, the hydrogen evolution experiments were repeated under dark using GeH/Pt (1.0 wt %)

as photocatalyst in H_2O/CH_3OH and under visible light irradiation containing only GeH powders. No hydrogen is generated in both cases as illustrated in Fig. 3b, indicating the generation of hydrogen is from the photocatalytic reaction instead of the decomposition of GeH.

To test the stability of GeH during photocatalytic reactions, cycling experiments were also carried out by repeated decomposing RhB dye for 10 times and H_2 evolution for 24 h (12h for once) under visible light ($\lambda \geq 420$ nm) irradiation. As shown in Fig. 3c, the photocatalytic activity of GeH is high even after repeated on decomposing RhB for 10 times with a slight decrease, which could be due to the loss of the samples during the recycling experiments. This decrease disappeared during the photocatalytic H_2 evolution experiments as shown in Fig. 3d. The H_2 evolution rate kept constant during the repeated experiments for 24 h, which indicated that the as-prepared GeH is stable and photo-reactive during photocatalytic experiments for a long time. The structures and morphologies of the samples after the two cycling experiments were also investigated by XRD and SEM (see Fig. S1 in the ESI†). And the samples kept their original structures and morphologies after the photocatalytic experiments, which further demonstrated that the as-prepared GeH samples are stable for photocatalytic applications.
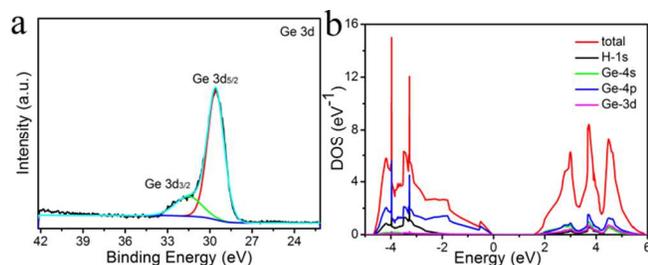

Fig. 4 (a) XPS spectra for Ge 3d of as-prepared GeH. (b) Calculated electronic DOS for GeH.

The band structure can provide more information for illustrating mechanism in photocatalytic reaction of semiconductors. XPS is a powerful tool to investigate the element composition. As shown in Ge 3d XPS (Fig. 4a), two peaks centered at 31.52 and 29.62 eV can be observed in the as-prepared GeH, which can attributed to the Ge $3d_{5/2}$ and $3d_{3/2}$, respectively. Compared with the Ge $3d_{5/2}$ and $3d_{3/2}$ positions of Ge metal,[17] the Ge $3d_{5/2}$ and $3d_{3/2}$ positions of samples have a higher binding energy, implying the existence of Ge-H bond indirectly.[18] To further understand the electronic structure of GeH, DOS was calculated and plotted in Fig. 4b. The DOS of Ge-H bond orbital and the anti-bonding orbital are both relatively dispersed, indicating the type of bond between them is mainly covalent bond. In the pure GeH, the valence band maximum (VBM) is mainly composed of Ge 4p orbitals and the conduction band minimum (CBM) composed of the Ge 4s, 4p, 3d and H 1s mixed state. The mixed state makes it possible that electrons are excited, thereby leading to the absorption of the visible light ($\lambda \geq 420$ nm). Based on the DFT calculations, GeH has a bandgap of 1.56 eV, which is close to our experimental result (1.58 eV) and previously reported value (1.59 eV)[9]. In addition, band position calculations (see the ESI†) suggest that GeH has the suitable energy potential (CB= -0.313 eV,

VB= 1.267 eV) which facilitates the transfer of the photo-excited carriers throughout the process of photocatalytic reaction. Based on experimental and theoretical results, a possible mechanism proposed to illustrate photocatalytic process of GeH. The electron on VB absorbed a photon with enough energy can transfer to CB, left a hole on VB, which have an oxidizing ability to decompose the organic pollutions. The electron on CB can diffuse from GeH to Pt on surface and subsequently react with the adsorbed H^+ ions to form H_2. Moreover, with methanol as scavenger, the generated holes can react with methanol rapidly, which restrained the recombination of carriers, resulting in the high efficiency of hydrogen evolution.

Conclusions

In summary, GeH with 2D layered structure was synthesized by a two-step method. With proper band structure, GeH exhibits photocatalytic activities in hydrogen evolution of water splitting and decomposition of RhB under irradiation of visible light ($\lambda \geq 420$ nm). Based on the experimental results and theoretical calculations, a possible mechanism was proposed to illustrate the photocatalytic process of GeH. The work demonstrated for the first time that GeH can be used as a novel visible light photocatalyst, which has great potentials on energy and environmental applications.

Notes and references

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† Electronic Supplementary Information (ESI†) available: Experimental details, Table S1, Figure S1. See DOI: 10.1039/c000000x/

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