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

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Experimental Details

Preparation of GeH

Ge, Ca, Pb, concentrated HCl and methanol were purchased and used without further purification. GeH products were prepared using a controlled and facile ion exchange approach described in previous report [1]. CaGe2 crystals used as precursor were synthesized by co-solvent method by using excess amount of Pb as a reactive flux. All manipulations were performed inside an argon-filled glove box with controlled oxygen and moisture levels below 1 ppm or under vacuum. The elements were commercially purchased and used as received: Ca (with purity > 99%, Aldrich), Ge (lump, 99.999%, Acros) and Pb (shot, 99.99%, Alfa-Aesar). The reactions were carried out by loading a mixture of the elements in a ratio of Ca:Ge:Pb = 1:2:25 in
alumina crucibles, and subsequently enclosing them in evacuated fused silica ampoules. The following temperature profile was employed: (1) heating to 1273 K at a rate of 300°/h; (2) homogenization at 1273 K for 20 h; and (3) slow cooling to 873 K at a rate of 3°/h. At this point, the evacuated silica ampoules were quickly removed from the furnace and centrifuged at the speed of 3,500 r/min, which were put upside down in the centrifuge, and then the Pb was separated from the reaction product. Further details on CaGe$_2$ crystals growth techniques can be found elsewhere [2]. The typical outcomes of such reactions were flake-shaped crystals with metallic luster. To synthesize GeH, the as-prepared CaGe$_2$ were mixed with concentrated HCl with constant stirring for 48 hours at -30°C. Then the product was separated and washed by deionized H$_2$O and methanol for three times, respectively. The GeH samples were obtained after dried in vacuum for 6 hours at room temperature.

**Characterization**

The powder X-ray diffraction (XRD) patterns were obtained by using a Bruker AXS D8 advanced X-ray powder diffractometer with Cu Kα radiation ($\lambda=1.54056$ Å) at room temperature. The morphologies of the samples were examined by scanning electron microscope (SEM) (Hitachi S-4800 microscope) and high-revolution transmission electron microscope (HRTEM) (JEOL JEM-2100). The diffuse reflectance spectrum was measured on a Hitachi U-4100 UV-Visible-NIR Spectrophotometers. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al Kα radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about $3\times10^{-10}$ mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

**Theoretical calculation**

The DFT calculations employed the projector augmented wave method coded in the Vienna ab initio simulation package [3], and the generalized gradient
approximation of Perdew-Burke-Ernzerhof (PBE) for exchange and correlation corrections [4] with plane wave cutoff energies of 400 eV, and a threshold of self-consistent-field energy convergence of $10^{-4}$ eV. The atomic positions were fully optimization until all the residual forces are smaller than 0.01 eV/Å. A Monkhorst–Pack k-point sampling was applied with a constant density corresponding to a $7\times7\times2$ k-point mesh for the structure of hexagonal GeH constructed on the basis of the 8-atom supercell with the lattice constant of $a=b=3.880\,\text{Å}$, and $c=10.211\,\text{Å}$, respectively.

**Photocatalytic measurements**

The photocatalytic performances of the as-prepared GeH were evaluated by decomposition of Rhodamine B (RhB) under visible light ($\lambda\geq420$ nm) irradiation at room temperature. A 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the light source and equipped with an ultraviolet cutoff filter to provide visible light ($\lambda\geq420$ nm). In a typical reaction, 50 mg of as-prepared GeH powders were dispersed in a Pyrex glass reactor (with a 30 cm$^2$ cross section and 5 cm height) containing 50 mL RhB solutions (with a concentration of 20 mg • L$^{-1}$). Prior to illumination, the suspension was kept in the dark with stirring for 30 min to obtain adsorption equilibrium. The concentration of RhB dye was measured by UV/Vis spectroscopy (UV-7502PC, Xinmao, Shanghai). For comparison, N-doped P25 was synthesized following the previously reported method [5], that is, by treating Degussa P25 in the NH$_3$ (67%)/Ar atmosphere at 550°C for 3 hours. The N concentration was 0.99 at% detected by XPS.

Photocatalytic hydrogen evolution reactions were carried out in a top-irradiation vessel connected to a glass-enclosed gas circulation system. In a typical procedure, 50 mg of catalyst was mixed with 100 ml aqueous solution containing 30 % methanol in volume with constant stirring. The reaction temperature was maintained at 5 °C. The amount of H$_2$ evolved was determined by using a gas chromatograph (Varian GC3800)
equipped TCD detector. The light source in the above photoreactivity experiment was a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd).

**Band position calculations**

For a compound, at the point of zero charge, the valence band (VB) position can be calculated by the following empirical formula [6]:

$$E_{VB} = X - E^e + 0.5E_g$$

where $X$ is the absolute electronegativity of the semiconductor, which is defined as the geometric mean of the absolute electronegativity of the constituent atoms, $E^e$ is the energy of free electrons on the hydrogen scale (ca. 4.5 eV), $E_{VB}$ is the VB edge potential and $E_g$ is the band gap of the semiconductor. The conduction band (CB) position can be deduced by $E_{CB} = E_{VB} - E_g$. Given the equations above, the top of the VB and the bottom of the CB of GeH are calculated to be 1.267 and -0.313 eV with respect to the normal hydrogen electrode (NHE), respectively.

The calculated band positions of GeH are summarized in Table S1.

**Table S1 Band energy positions of GeH.**

<table>
<thead>
<tr>
<th>semiconductors</th>
<th>electronegativity ($X$)</th>
<th>estimated $E_g$ (eV)</th>
<th>calculated VB position (eV) vs.NHE</th>
<th>calculated CB position (eV) vs.NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH</td>
<td>4.977</td>
<td>1.58</td>
<td>1.267</td>
<td>-0.313</td>
</tr>
</tbody>
</table>
References:


Fig. S1 a) XRD patterns of GeH samples. 1#: fresh, 2#: after H₂ evolution twice and 3#: after degradation of RhB for 10 times. SEM images of GeH samples b) fresh, c) after H₂ evolution twice and d) after degradation of RhB for 10 times.