Electronic Supplementary Material (ESI) for Chemical Communications

This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information (ESI)

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

Zhenhua Liu,[a] Zaizhu Lou,[a] Zhujie Li,[b] Gang Wang,[a] Zeyan Wang,[a] Yuanyuan Liu,[a] Baibiao Huang,*[a] Shengqing Xia,*[a] Xiaoyan Qin,[a] Xiaoyang Zhang,[a] and Ying Dai[b]

a *State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, P. R. China,*

Email: bbhuang@sdu.edu.cn, shqxia@sdu.edu.cn. Fax: (+86) 531-8836-5969.

b *School of Physics, Shandong University, Jinan 250100, P. R. China.*

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]. $CaGe_2$ 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℃. Then the product was separated and washed by deionized H_2O 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 (λ= 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 3×10^{-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 7×7×2 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=3.880Å, and c=10.211Å, respectively.

Photocatalytic measurements

The photocatalytic performances of the as-prepared GeH were evaluated by decomposition of Rhodamine B (RhB) under visible light ($\lambda \geq 420$ 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 ($\lambda \geq 420$ 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 $mg \cdot L^{-1}$). 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]:

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

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 Eg is the band gap of the semiconductor. The conduction band (CB) position can be deduced by $E_{CB} = E_{VB} - Eg$. 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.

semiconductors	electronegativity (X)	estimated Eg(eV)	calculated VB position (eV) vs.NHE	calculated CB position (eV) vs.NHE
GeH	4.977	1.58	1.267	-0.313

References:

1 E. Bianco, S. Butler, S. S. Jiang, O. D. Restrepo, W. Windl and J. E. Goldberger, *ACS Nano.*, 2013, **7**, 4414.

2 P. H. Tobash, S. Bobev, *Journal of Solid State Chemistry*, 2007, **180**, 1575.

3 G. Kresse, J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15; G. Kresse, J. Furthmüller, *Physical Review B*, 1996, **54**, 11169.

4 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Physical Review B*, 1992, **46**, 6671; J. P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865.

5 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269.

6 Y. Xu and M. A. A. Schoonen, *Am. Mineral.*, 2000, **85**, 543; H. F. Cheng, B. B. Huang, Y. Dai, X. Y. Qin and X. Y. Zhang, *Langmuir*, 2010, **26**, 6618.

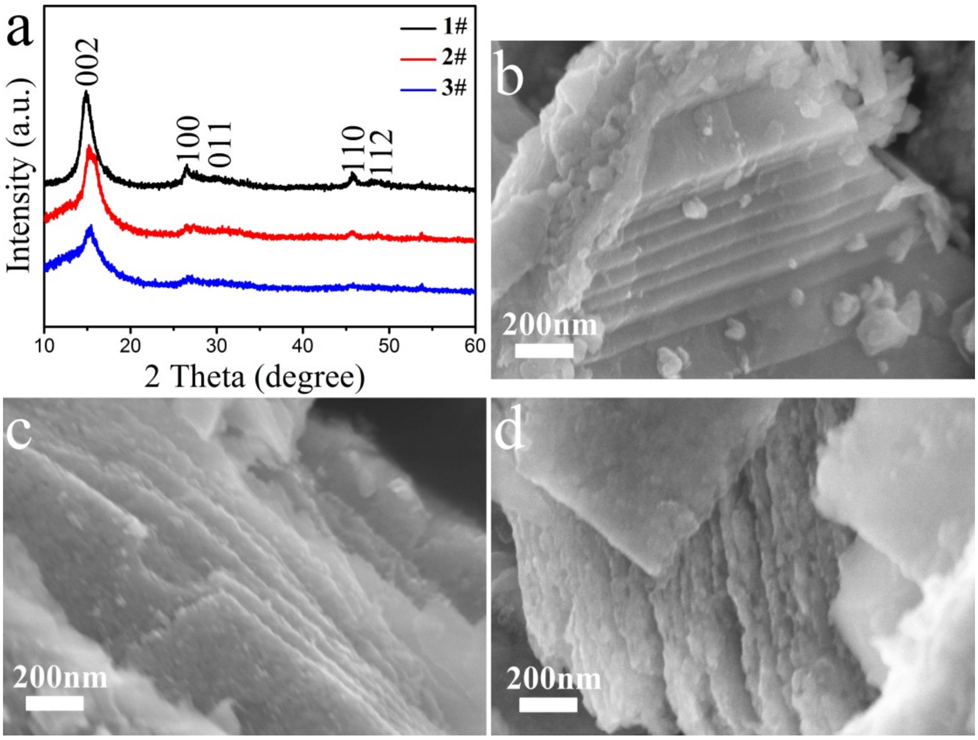

Fig. S1 a) XRD patterns of GeH samples. 1#: fresh, 2#: after H_2 evolution twice and 3#: after degradation of RhB for 10 times. SEM images of GeH samples b) fresh, c) after H_2 evolution twice and d) after degradation of RhB for 10 times.