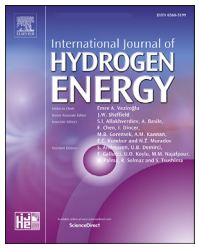
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–10

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



New gallium chalcogenides/arsenene van der Waals heterostructures promising for photocatalytic water splitting

Qiong Peng [a], Zhonglu Guo [a], Baisheng Sa [b,*], Jian Zhou [a], Zhimei Sun [a,**]

[a] School of Materials Science and Engineering, and Center for Integrated Computational Materials Science, International Research Institute for Multidisciplinary Science, Beihang University, Beijing, 100191, China

[b] Multiscale Computational Materials Facility, Key Laboratory of Eco-materials Advanced Technology, College of Materials Science and Engineering, Fuzhou University, Fuzhou 350108, China

ARTICLE INFO

Article history:
Received 18 September 2017
Received in revised form
30 June 2018
Accepted 4 July 2018
Available online xxx

Keywords:
vdW heterostructures
Photocatalytic water splitting
Band structure engineering
Enhanced optical absorption
High carrier mobility

ABSTRACT

Single two-dimensional (2D) GaS and GaSe were studied as photocatalysts, yet the overall performance is limited by the low optical absorption and inefficient separation of photogenerated electron-hole pairs. Constructing van der Waals (vdW) heterostructures is an ideal way to overcome the deficiency of single 2D gallium chalcogenides. This work unravels that gallium chalcogenides/arsenene (GaX/As, X = S, Se) are the promising vdW heterostructures that show significantly improved photocatalytic performance by means of first-principles calculations. The GaX/As heterostructures possess suitable band alignment and bandgap satisfying the requirements for photocatalysts. Contrary to the pristine monolayers, the $Se_{0.5}GaS_{0.5}$/As and $S_{0.5}GaSe_{0.5}$/As heterostructures undergo indirect-direct bandgap transition by varying the interlayer distances; moreover, they exhibit high carrier mobility (~2000 $cm^2 V^{-1} s^{-1}$ for electrons) and transport anisotropy, efficiently facilitating the migration and separation of photogenerated electron-hole pairs. Finally, all GaX/As heterostructures show significantly enhanced optical absorption beyond the isolated GaX monolayers under visible-light irradiation. These extraordinary properties render GaX/As heterostructures as competitive photocatalysts for water splitting to produce hydrogen.

Introduction

Hydrogen production by photocatalytic water splitting is an environmentally friendly, nonpolluting and endless renewable source of clean energy via utilizing solar energy [1–3]. The semiconductor photocatalysts should fulfill the basic requirements, including appropriate band gaps and band alignments, widespread availability, and efficient separation of photogenerated electron-hole pairs [4,5]. Searching for efficient photocatalysts for water splitting under visible light irradiation, however, remains one of the most challenging tasks [6–9]. Inspired by the experimental realization of graphene [10], two-dimensional (2D) atomically thin group-III monochalcogenides, such as GaS, GaSe and InSe, have been widely studied as photocatalysts and successfully synthesized by various methods including mechanical cleavage, solvent exfoliation and pulsed laser deposition from their bulk phases

* Corresponding author.
** Corresponding author.
E-mail addresses: bssa@fzu.edu.cn (B. Sa), zmsun@buaa.edu.cn (Z. Sun).

https://doi.org/10.1016/j.ijhydene.2018.07.008
0360-3199/

[11–14]. The 2D GaS and GaSe crystals are composed of vertically stacked S–Ga–Ga–S and Se–Ga–Ga–Se sheets in one unit cell, respectively. They are intrinsic *p*-type semiconductors [14,15], which are superior to *n*-type transition metal dichalcogenides (TMDs) for electronic devices [16]. Meanwhile, because of the quantum confinement effect, 2D GaS and GaSe crystals exhibit many fascinating properties, such as tunable magnetism [17] and magneto-optical effects induced by hole doping [18], as well as tunable electronic and dielectric behavior by varying the number of layers or applying mechanical strain [19], and so on. Yet their low optical absorption and unwanted recombination of photogenerated charge carriers greatly limit their practical application in photocatalytic water splitting [20,21].

Structural symmetry-breaking of Janus monolayer plays a crucial role in improving the electronic structures and piezoelectric properties of 2D materials [22,23]. It is worth noting that a series of derivative Janus structures of group-III monochalcogenides ($GaS_{0.5}Se_{0.5}$, $InS_{0.5}Se_{0.5}$, $Ga_{0.5}In_{0.5}S$, etc) were theoretically confirmed to possess great thermodynamic and dynamic stability [23]. Considering the fact that the Janus structure of MoSSe has been successfully synthesized through H_2 plasma stripping and thermal selenization methods [22], it is reasonable to expect that the Janus structures of group-III monochalcogenides can be obtained by the similar means. On the other hand, constructing van der Waals (vdW) heterostructures is also an effective way to modulate the electronic properties, which is achieved by combining two or more 2D materials together through interlayer vdW forces [24–26]. Graphene-like 2D materials provide an ideal platform for creating vdW heterostructures with unprecedented characteristics or unique functionalities [27]. Tremendous efforts have been devoted to exploring and fabricating GaX-based (X = S, Se) vdW heterostructures, such as GaSe/graphene [28,29], GaSe/n-InSe [30], GaS/GaSe [31], GaSe/$MoSe_2$ [32], etc. Importantly, the interlayer interactions are controllable directly by modifying the interlayer separation [33,34].

Recently, Zhang et al. proposed a new class of 2D materials, namely arsenene (As) and antimonene (Sb) [35], which shows wide indirect bandgaps, high stability, anomalous negative Poisson's ratio and high hole mobility of 1700 $cm^2\ V^{-1}\ s^{-1}$ [36–39]. Notably, arsenene and GaX monolayers share the similar hexagonal lattice structures and constants. Constructing GaX/As vdW heterostructures is highly anticipated to combine the advantages of these two materials and potentially gives rise to improved performance. In this work, we employ the first-principles calculations to extensively investigate the related properties of GaX/As vdW heterostructures and reveal their potential applications as highly efficient visible-light photocatalysts for water splitting. Importantly, the $Se_{0.5}GaS_{0.5}$/As and $S_{0.5}GaSe_{0.5}$/As heterostructures not only exhibit tunable direct bandgap, but also possess high and directionally anisotropic carrier mobility coupled with very good optical absorption in visible-light wavelengths, which would contribute to the migration and separation of photogenerated electron-hole pairs, and then facilitate the redox reaction of water to form hydrogen on the semiconductor surface. This is the mostly desirable photocatalysis performance in practice [40], which however was rarely achieved previously. Our findings will accelerate the application of group-III monochalcogenides in photocatalytic water splitting, and further guide the design of more 2D semiconductors for photocatalysis.

Methods

DFT calculations

All the density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP) [41]. We adopted the projector-augmented wave (PAW) potentials for describing the ion-electron interaction [42], the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) for exchange-correlation interactions between electrons [43]. The DFT-D2 method was employed in the following calculations for GaX/As heterostructures because of its good description in long-range vdW interactions [44]. which yields fairly good results for bulk β-GaS, ε-GaSe (Table S1) as compared to the experimental data [45,46]. The cut-off energy was set to 500 eV. A vacuum space of 20 Å in the z direction was constructed to avoid the interactions between neighboring slabs. All the geometry structures were fully optimized in terms of atomic positions and lattice parameters, until the energies and forces were converged to 10^{-5} eV and 0.01 eV/Å, respectively. The HSE06 [47] hybrid density functional combined with DFT-D2 was used to calculate the bandgaps. The amount of charge transfer was estimated quantitatively using Bader charge analysis [48]. To obtain accurate dielectric functions, we used the time-dependent Hartree-Fock calculations (TDHF) based on the HSE06 calculations, which takes excitonic effects into account [49].

Carrier mobility calculations

The carrier mobility was estimated based on the deformation potential theory as follows [50]:

$$\mu_{2D} = \frac{2e\hbar^3 C_{2D}}{3\kappa_B T|m^*|^2 E_i^2}, \quad (1)$$

where e, $\hbar$, k_B and T are the electron charge, reduced Planck constant, Boltzmann constant and temperature, respectively. The temperature of 300 K was adopted. E_i is the deformation potential constant, defined as $E_i = \partial E_{edge}/\partial\varepsilon$, where E_{edge} is the band edge energy of CBM and VBM induced by uniaxial strain. And $C_{2D} = (\partial^2(E - E_0)/\partial\varepsilon^2)/S_0$ is elastic modulus, where $E–E_0$ is the total energy shift activated by strain effect and S_0 is the equilibrium area. The effective masses m^* of electrons (m_e^*) and holes (m_h^*) are obtained by $m^* = \hbar^2(\partial^2 E/\partial k^2)^{-1}$, i.e., a stronger dispersion of the band suggests a smaller m_i^* for carriers.

Results and discussion

Structural stability

The optimized lattice constants of GaS, GaSe, Janus $GaS_{0.5}Se_{0.5}$ and arsenene monolayers are 3.636, 3.811, 3.724 and 3.608 Å, respectively, which coincide with the available data [31,51], as

Please cite this article in press as: Peng Q, et al., New gallium chalcogenides/arsenene van der Waals heterostructures promising for photocatalytic water splitting, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.07.008