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Two-dimensional group-VA porous crystals: Diverse electronic structures and photocatalytic properties

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ABSTRACT

The two-dimensional materials (2D) have been widely investigated due to their unique properties. In this paper, based on DFT calculations, a family of novel 2D group-VA porous crystals have been explored, which are named as T-VA (VA = P, As, Sb, and Bi) due to the tetragonal lattice. Their thermal stability has been carefully confirmed due to careful phonon calculations. These 2D materials possess high specific surface area due to big intrinsic porous crystals, making them good candidates for catalysts. More importantly, they are semiconductors with wide band gap range of 0.94–2.78 eV (HSE06 level) and also exhibit considerable absorption index on both visible and infrared regions of solar energy as well as suitable band alignments for photocatalytic water-splitting. Such results reveal a group of novel 2D materials based on group-VA elements which are expected to be fabricated and utilized as nanoelectronics and photocatalysts.

1. Introduction

Two-dimensional (2D) materials, sometimes referred to as single or several-layer materials, have captured the fascination of a steadily increasing number of scientists. These materials can exhibit unique physical properties due to quantum confinement effects [1,2]. Over the past three years, 2D group-VA materials have attracted lots of interests due to the superior hole mobility, such as 10000 $cm^2 V^{-1} s^{-1}$ of black phosphorene [3,4]. These 2D group-VA materials possess a wide band gap range, and extremely high carrier mobility [5,6]. More importantly, these 2D nanosheets with diverse layers have been fabricated experimentally by various methods [7–10].

Beyond perfect honeycomb lattice, a special family of 2D porous materials have also been focused on. Early from 2010, many porous graphene allotropes have been reported [11], such as T-graphene [12] with Tetrarings, porous graphene (biphenylene carbon) [13] and (R-graphyne) with tetra-rings and acetylenic linkages [14], which possess distinct electronic structures with graphene. Besides carbon allotropes, other 2D porous monolayers have also been reported, which can also be potential applications in hydrogen storage (e.g. porous BN [15,16]) and single atom catalysis (g-C_3N_4 [17], C_2N monolayers [18] and 2D organic semiconductors [19]) due the extremely high specific surface area.

The 2D group-VA materials belongs to either α- or β-phases or their compounds. So far, some porous 2D group-VA nanomaterials have been reported. In 2016 and 2018, twenty-one new porous 2D phosphorous allotropes and three porous 2D nanosheets (pSiP, pSiAs and pSiSb) are reported due to theoretical calculations, respectively [20,21]. In this paper, by density functional theory (DFT) calculations, four porous 2D crystals are explored, which are referred as T-VA (VA = P, As, Sb, and Bi) due to tetragonal lattice. Furthermore, the potential utilization in electronic and photocatalytic industry has been declared due to the calculated electronic and optic properties.

2. Methods

The density functional theory (DFT) calculations were performed with the Vienna Ab Initio Simulation Package (VASP) [22,23]. Projector-augmented-wave (PAW) potentials [24] were used to account electron-ion interactions. The generalized gradient approximation (GGA) with the PBE functional [25] was used to treat the electron exchange correlation interactions. To remove spurious interactions between neighboring structures due to periodic calculations, a vacuum layer of no less than 15 Å was taken in the perpendicular direction when necessary. The energy cutoff was set to 400 eV and Monkhorst-Pack scheme was used to sample Brillouin zone (BZ) [26] with 9 × 9 × 1 K-meshes. The equilibrium geometries were fully optimized with both the lattice vectors and atom coordinates relaxed with the tolerance of less than 0.01 eV/Å on each atom. The phonon calculations

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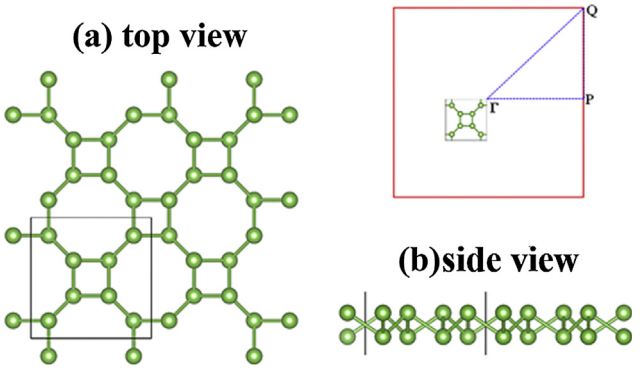

Fig. 1. (a) and (b) top and side views of atomic structure of 2D T-As crystals. The inset displays the Brillouin zone and high-symmetry k-points defining the directions in the following phonon and electronic band structures.

Table 1
The structure parameters of porous 2D group-VA crystals. The lattice constant a, bond length l and vertical layer thickness h are given in Å and the cohesive energy ΔE_c is given in eV/atom.

	T-P	T-As	T-Sb	T-Bi
a	6.46	7.13	8.16	8.60
l	*2.27*	*2.51*	*2.90*	*3.06*
h	*1.25*	*1.41*	*1.65*	*1.74*
ΔE_c	5.212	4.521	3.927	3.655

were performed by using the Phonopy package [27]. The real-space force constants were calculated from the Hellmann-Feynman forces by introducing displacements to supercells based on finite displacement method [28], and the dynamical matrices and phonon frequencies were obtained via the force constants.

3. Results and discussion

3.1. Structure and stability

The optimized 2D crystals belong to 100.P4bm(C_{4V}-2) point group symmetry, as shown in Fig. 1, which contains alternating square and octagonal rings. The porous crystals have a tetragonal lattice and consequently names as T-VA (VA = P, As, Sb, and Bi). The lattice constants increase with atom number increases, as well as the bong length and vertical layer thickness. Clearly, all materials share the buckled structures with ordinay*2D group-VA* α- or β-phases by lowing total energy. Furthermore, the layer thickness also increase when VA change from phosphorus to bismuth.The cohesive energy of these porous crystals is calculated by $\Delta E_c = E(\text{VA}) - E(\text{T-VA})$ to determine their thermal stability, where $E(\text{VA})$ and $E(\text{T-VA})$ represent total energy of isolated VA atom (VA = P, As, Sb, and Bi) and that of T-VA crystals per each atom, respectively. The minimum cohesive energy is 3.66 eV/atom for T-Bi, while the maximum value is 5.21 eV/atom for T-P, as shown in Table 1. The cohesive energy of present 2D crystals is in the same order with that (6.37 eV) [29] of 2D single-layer MoS_2, which has been successfully synthesized by many methods such as micromechanical exfoliation [30].

The phonon dispersion spectrum analysis is a reliable tool to confirm the structure stability. If all phonon frequencies on the k-points in

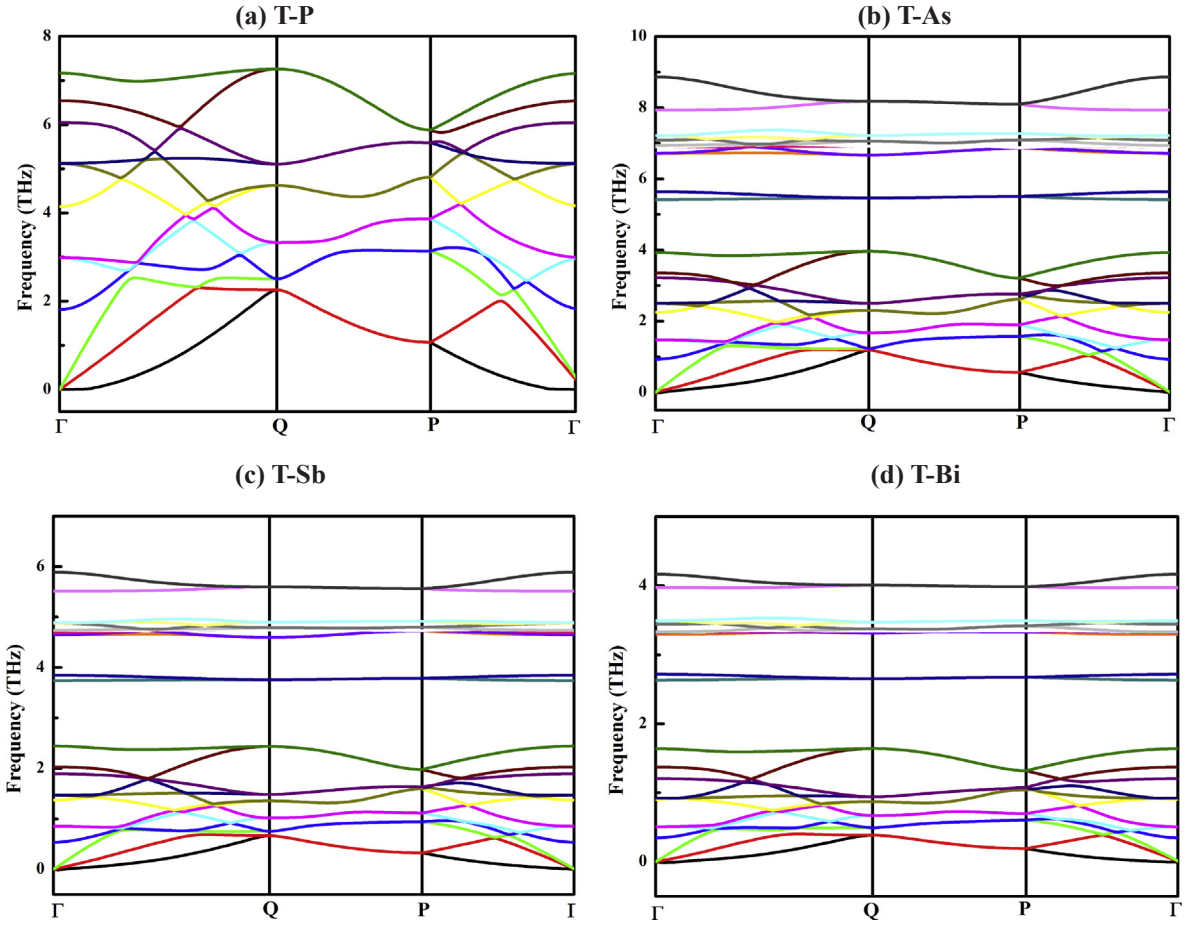

Fig. 2. The phonon dispersions of porous 2D group-VA crystals.