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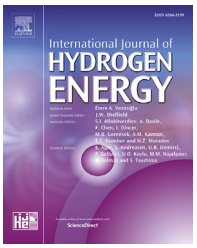

Electronic structure and hydrogen storage properties of Li–decorated single layer blue phosphorus

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ABSTRACT

Single layer blue phosphorus (SLBP) is a promising two–dimensional material for nanoelectronic devices, but the electronic structure and hydrogen storage property of modified SLBP received little attention. Li atoms can be strongly bonded on SLBP in a 1:1 Li/P ratio with a binding energy larger than the cohesive energy of bulk Li. The geometric structure of SLBP suggests the 3s3p orbitals of the P atom hybridize in sp^3 manner. But our analyses show that the 3s and 3p orbitals form bonding and antibonding orbitals respectively. The 3s orbitals are fully occupied as they have much lower energies, and the bonding orbitals formed by P 3p are occupied in pure SLBP. The decorated Li atoms transfer their 2s electrons to the antibonding orbital formed by P 3p. The Li atoms exist as +1 cations and they are ionically bonded on SLBP. H_2 molecules adsorbed on the Li^+ cations are strongly polarized and form strong adsorption. When two H_2 are adsorbed on each Li atom decorated at the 1:1 Li/P ratio, the hydrogen storage capacity reaches 9.52 wt% but the H_2 molecules are arranged in two layers with the adsorption energy −0.168 eV/H_2. When the Li atoms are decorated alternatively on the two sides of the P_6 rings with a Li/P ratio of 1:2, each Li atom can absorb two H_2 molecules in a single–layer; the hydrogen storage capacity is 5.48 wt% and the adsorption energy reaches −0.227 eV/H_2. These results mean the Li–decorated SLBP can work at ambient temperature with high reversible hydrogen storage capacity.

Introduction

The extensive consumption of fossil fuels leads to rapid depletion of these resources, and the greenhouse gas emissions pose serious threats to our living environment. Providing clean and renewable energy sources is one of the key technological challenges facing mankind. Hydrogen is considered as the most promising candidate to solve the globe's energy problems as it has the highest heating value per mass and the combustion product is only water. However, the storage technique is a bottleneck for fuel–cell–based light–duty vehicles [1–3]. To overcome this difficulty, great efforts must be made to find materials with high storage capacity and suitable uptake–release kinetics. The technical targets set by the US Department of Energy for 2020 are 5.5 wt % gravimetric density at operating temperatures −40–60 °C with a charging/discharging rate of 1.5 kg H_2/min [4]. The

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binding energy for the ideal hydrogen storage materials changes considerably in the literature; it falls in the range of −0.2–0.6 eV per H_2 molecule [5–11]. Up to now, no materials have been found to reach a satisfactory level for the hydrogen storage because hydrogen molecules interact either too weakly (physisorption) or too strongly (chemisorption) with the host materials.

Thanks to the extraordinary physical and chemical properties, two–dimensional (2D) materials has become one of the most rapidly developing areas of condensed matter physics and material science, especially in hydrogen storage [12–18]. To increase the adsorption energy of hydrogen molecule and the storage capacity, feasible methods are decorating metal atoms on the 2D materials. H_2 molecules can be adsorbed via electrostatic interaction on Li, Mg, Al, etc. atoms or via Kubas interaction on transition metals [19–29]. For example, Ataca et al. found that Li decorated graphene has a high hydrogen storage capacity (12.8 wt%) [21]. The hydrogen storage properties of calcium decorated 2D carbon allotropes, including C_{40}, C_{41}, C_{63}, C_{64} and C_{65}, were studied by Pan et al., and the results showed that Ca–decorated C_{64} can produce a hydrogen density of 8.57 wt% [26]. Ti–decorated graphene under a 10% tensile strain was also regard as efficient hydrogen storage materials, and the storage capacity can reach 9.50 wt% [28]. However, the decorating of metal atoms on most 2D materials suffers from low binding energies, which will lead to the clustering of decorated metals on the host.

As a new kind of stable 2D materials, the blue phosphorus has received a lot attention in the nanoelectronic device because of its specific honeycomb geometric structure and tunable band gaps [30,31]. The single layer blue phosphorus (SLBP) was first predicted through density functional theory (DFT) calculations [32] and then successfully synthesized by molecular beam epitaxial growth on Au (111) using black phosphorus as precursor [33]. Experimental and theoretical studies found that the structure of SLBP is closer to silicone, which has slightly flatter "zigzag" ridges other than the deeper "armchair" ridges of black phosphorus. Unlike graphene as a zero–gap 2D material, the blue phosphorus possesses tunable band gaps from 2.0 eV for SLBP to about 1.2 eV for the bulk. Compared with 2D MoS_2, the SLBP enjoys a much improved carrier mobility [34–39]. It was also found that the nonmetal–atom doped SLBP showed superior electronic and magnetic properties [40]. Although the SLBP has great potential in nanoelectronic devices, the hydrogen storage properties of SLBP receive little notice.

Li et al. found that Li–decorated SLBP exhibits superior electronic properties as an anode material for lithium–ion batteries [41]. Considering the light weight and low ionization potential of Li atom, Li–decorated SLBP could be an excellent hydrogen storage material. In this work, we study the electronic structure and hydrogen storage properties of Li–decorated SLBP by density functional theory. The results show that the Li atoms can interact strongly with the SLBP to keep them dispersed. The state of the decorated Li is close to the +1 cation and the adsorbed hydrogen molecules can be strongly polarized by the Li^+ ions. When the Li/P ratio is 1:1 and two H_2 molecules are adsorbed on each Li atom, the hydrogen storage capacity reaches 9.52 wt% but the molecules form two layers with an average adsorption energy −0.168 eV/H_2. When the Li atoms are decorated alternatively at the two sides of the P_6 rings with a Li/P ratio of 1:2, each Li atom can adsorb two H_2 molecules with a hydrogen storage capacity of 5.48 wt% and the adsorption energy can reach −0.227 eV.

Calculation method

DFT calculations are performed using the Vienna *ab initio* simulation package (VASP) [42,43]. The projected augmented wave (PAW) method is employed [44]. The exchange–correlation interactions are expressed with the generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) functional [45]. Van der Waals (vdW) interaction is important for the adsorption of H_2 molecules, we include it by using the empirical correction scheme of Grimme (DFT + D2) [46]. The energy cutoff for expansion of wave functions is 500 eV. The Brillouin zone is sampled with 3 × 3 × 1 for (4 × 4) supercell by Monkhorst–Pack k–point scheme. The Gauss function with $\sigma = 0.2$ eV is adopted for the smearing method. The interlayer distance is set at 50 Å to avoid the interaction between the layers. The convergence criterion of 10^{-5} eV for energies has been used, and geometry optimization is performed until the force acting on each ion become less than 10^{-2} eV/Å. Our test calculations show that the above parameters offer reliable convergence. Finite clusters $P_{24}H_{12}$ and $P_{24}Li_{26}H_{12}$ are calculated by using the density functional theory with Becke's three–parameter exchange functional and Lee–Yang–Parr correlation functional (B3LYP) [47]. The double–zeta split basis sets with polarization functions 6–31G (d,p) are employed. The computations are performed using Gaussian 09 program [48].

Results and discussion

Structure of SLBP

Fig. 1 shows the top and side views of the 4 × 4 supercell of SLBP, which presents a specific honeycomb structure. The optimized lattice constant is 3.28 Å. The honeycomb net is formed by two interpenetrating triangle sublattices (shown in

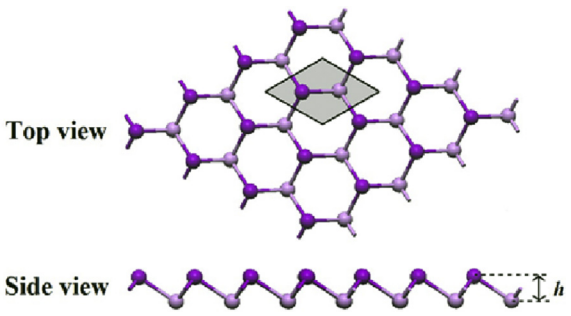

Fig. 1 – Top and side views of a 4 × 4 supercell of SLBP. The shaded area represents the unit cell. Atoms in the top and bottom layers, which form two interpenetrating triangular sublattices, are distinguished by light and dark colors.

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