Surface functionalization of phosphorene via P–H bond for ambient protection and robust photocatalytic H₂ evolution

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ABSTRACT The facile oxidation of few-layer black phosphorus (i.e., phosphorene) in the atmospheric environment is a major hurdle for its applications in photocatalytic solar-energy conversion. The introduction of protective layers, such as a surface capping layer, surface coordination, and P–C covalent functionalization, can protect phosphorene from oxidative degradation but inevitably decreases its photocatalytic performance due to the blockage of catalytic active sites. Herein, we develop a hydrogenation approach *via* the introduction of P–H covalent bonds on the surface of phosphorene (i.e., phosphorene-H) to inhibit the oxidation of phosphorene-H without sacrificing the original photocatalytic H₂ evolution performance. Experiments and density functional theory calculations demonstrate that about 5 mol% of phosphorus atoms in phosphorene-H are involved in forming P–H covalent bonds, hindering the reaction between O₂ and phosphorene-H in terms of thermodynamics and kinetics. This hydrogenation strategy is envisaged to augment the prospect of phosphorene in the field of photocatalysis.

Keywords: phosphorene, antioxidation, hydrogenation, photocatalytic H₂ evolution

INTRODUCTION

Phosphorene has been gaining prominence as a promising candidate for next-generation photoelectronic materials [1–4]. The tunable intrinsic bandgap, highly anisotropic carrier transport, and optical response properties allow this two-dimensional (2D) material to have great potential in the field of photocatalytic solar energy conversion [5,6]. However, the vulnerability of the lone pair on phosphorene to oxidation by electrophilic reagents limits phosphorene's stability in the presence of O₂ and water [7–10], which undermines its practicability in practical applications. It is generally believed that the oxidation reaction is initiated upon contact of O₂ on the phosphorene surface, followed by removal of P_xO_y from the surface and exposure of P⁰ for further oxidation [11–14]. In order to address this intrinsic shortcoming, surface capping layers including graphene, hexagonal boron nitride, and aluminum

oxide layers have been harnessed to protect phosphorene against O₂ and water [9,15–17]. Additionally, chemical modification methods, such as surface coordination and P–C covalent functionalization, have also been employed to improve the stability of phosphorene [18–25]. Although these strategies prevented oxidation-induced degradation and enabled its successful application in field-effect transistors, the presence of protective layers on the surface of phosphorene inevitably decreased its photocatalytic performance due to the blockage of catalytic active sites. Therefore, developing a novel approach to achieve high stability and photocatalytic activity simultaneously is desired for advancing the application of phosphorene in photocatalysis.

Hydrogenation has been demonstrated as a powerful tool in silicon technology to realize surface passivation [26]. We conceive that it could be a promising protection strategy for improving phosphorene's robustness in the course of photocatalysis which has not been explored. In this work, we developed a strategy for surface hydrogenation and passivation of phosphorene *via* the introduction of P–H covalent bonds to enhance the stability of the resulting phosphorene-H towards ambient air and water. Importantly, phosphorene-H maintained high photocatalytic performance after hydrogenation. Experiments and density functional theory (DFT) calculations demonstrated that about 5 mol% of phosphorus atoms in phosphorene-H were involved in forming P–H covalent bonds, hindering the reaction between O₂ and phosphorene-H in terms of thermodynamics and kinetics. In the meantime, the presence of 5 mol% coverage of P–H covalent bonds did not affect the carrier mobility compared with that of pristine phosphorene. As far as we know, few cases of high stability and excellent photocatalytic performance based on phosphorene material are achieved simultaneously in the ambient environment.

EXPERIMENTAL SECTION

Chemical and materials

All materials were of analytical grade and used as received without further purification. Bulk black phosphorus powders (>99.998%) were purchased from Nanjing XFNANO Materials

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TECH CO., Ltd. *N*-methyl-2-pyrrolidone (NMP), methanol, and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd.

Syntheses of phosphorene and phosphorene-H

Bulk black phosphorus powders (30 mg) were added into 50 mL of NMP solution, which was sonicated for 6 h using a tip sonicator at about 0°C. Subsequently, the dispersion was centrifuged at 6000 r min⁻¹ for 10 min to remove unexfoliated bulk black phosphorus and collect the supernatant. Then, the supernatant was further centrifuged at 12,000 r min⁻¹ for 30 min to collect phosphorene. Afterward, phosphorene was washed with ethanol five times and dried in a vacuum oven at 40°C for further usage.

The hydrogenation of phosphorene was carried out in a tube furnace filled with a gas mixture of ultra-high purity hydrogen and argon under atmospheric pressure; the flow rate of hydrogen gas and argon was 1 and 10 standard cubic centimeter per minute (sccm), respectively. Phosphorene was annealed at 350°C for 4 h with a heating rate of 3°C min⁻¹; the obtained sample was denoted as phosphorene-H.

Photocatalytic activity measurement

Photocatalytic H₂ evolution was performed in a 50-mL quartz tube sealed with a silicone rubber septum. In a typical photocatalytic experiment, 1 mg samples were dispersed in 30 mL of methanol-H₂O solution ($V_{\text{methanol}}:V_{\text{water}} = 1:9$). The system was then deoxygenated with Ar for 30 min to remove the air before irradiation. A light-emitting diode (LED) (100 W, $\lambda > 420$ nm) was used as the irradiation light source, and its irradiation spectrum is shown in Fig. S1. The quantities of H₂ evolution were measured using a gas chromatograph (GC-2014C, Shimadzu) with Ar as the carrier gas, which was equipped with a 5-Å molecular sieve column (3 × 2 mm²) and a thermal conductivity detector.

Materials characterization

The purity and crystallinity of the as-prepared samples were characterized by X-ray diffraction (XRD) on a Bruker D8-advance diffractometer using Cu K ($\lambda = 1.54056$ Å). The XRD data for indexing and cell-parameter calculation were collected in a scanning mode with a step length of 0.1° and a preset time of 1 s/step. Morphologies of samples were examined with transmission electron microscopy (TEM) with a JEM 2100F field emission gun transmission electron microscope operated at an accelerating voltage of 200 kV. The high-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained using a Titan 80-300 STEM operated at 300 kV, equipped with a probe spherical aberration corrector. Furthermore, Raman measurements were performed using a Renishaw inVia-Reflex spectrometer equipped with a notch filter, charge coupled device detector, and a 532-nm laser. The spatial Raman mapping was obtained by monitoring the intensity of A_g¹ mode of phosphorene and phosphorene-H (0.5 μm lateral resolution, 0.25 s exposure). The sample absorbance was measured using a UV-vis absorption spectrometer (U-3010). Chemical characterization of the sample's surface was performed with X-ray photoelectron spectroscopy (XPS, ThermoFisher ESCALAB 250Xi). Moreover, the charge effect was calibrated using the binding energy of C 1s. Nonmetal elemental analyses were performed *via* an Elementar Vario MACRO cube.

Fourier-transformed infrared (FTIR) data were collected at an ambient temperature on a Bruker ALPHA FTIR spectrometer from 4000 to 400 cm⁻¹. Atomic force microscopy (AFM) experiments were acquired using a Bruker Multimode 8 scanning probe microscope (Veeco, USA) to monitor the degradation process of the sample. The samples were prepared by drop-casting suspension on a SiO₂/Si (200 nm) substrate and fast-dried within 1 h under a vacuum. Subsequently, the samples were kept in ambient air at room temperature for different durations.

Computational methods

The first-principles calculations were performed with the plane-wave pseudopotential method implemented in CASTEP based on DFT [27–29]. Additionally, the exchange-correlation (XC) functions were described by the local density approximation (LDA) [30], and ultrasoft pseudopotentials were utilized to model the ion-electron interactions for all constituent elements [31]. A kinetic energy cutoff of 340 eV and Monkhorst-Pack *k*-point meshes spanning less than 0.04/Å³ in the Brillouin zone were chosen to ensure sufficient accuracy [32]. Meanwhile, the atomic position in the unit cell of compounds was fully optimized using the quasi-Newton method [33]. The convergence thresholds between optimization cycles for energy change, maximum force, maximum stress, and maximum displacement were set as 5.0 × 10⁻⁶ eV per atom, 0.01 eV per Å, 0.02 GPa, and 5.0 × 10⁻⁴ Å, respectively. The optimization terminated when all of these criteria were satisfied.

RESULTS AND DISCUSSION

Synthesis and characterization of phosphorene-H

Phosphorene was prepared by exfoliating black phosphorus crystals in NMP [34]. Then, the obtained phosphorene was annealed in a hydrogen atmosphere to form phosphorene-H. The plausible structure after energy optimization based on DFT calculations is presented in Fig. 1a. When two hydrogenation sites exist in the designed supercell of 36 phosphorus atoms (about 5 mol% of H atom), the calculated formation energy is approximately -8.3 eV, signifying the hydrogenation on the phosphorene surface through the formation of a P-H covalent bond is thermodynamically favorable. Moreover, introducing the P-H covalent bond leads to slight lattice distortion as P atoms adopt a four-coordinate geometry.

TEM and HAADF-STEM were first conducted to identify the effect of hydrogenation on the morphology and atomic configuration of phosphorene. As shown in TEM images (Fig. S2), the morphology and size of phosphorene remained unchanged after hydrogenation treatment. However, the difference in atomic configuration is pronounced when the images are enlarged (Fig. 1b–d). The atomic columns of phosphorene-H were significantly distorted after hydrogenation treatment compared with phosphorene having exact atomic column positions viewed along the [010] orientation, which is consistent with the DFT calculation results. Meanwhile, a ~2% lattice expansion was observed from the increased lattice distances of (200) facets (from 1.68 to 1.72 Å), as displayed by the line profiles displayed in the insets. Atomic configuration distortion and lattice expansion could act as a strong indicator for the existence of P-H covalent bonds. Furthermore, the 3V₂ (A₁) vibration mode of the P-H bond located at 2923 cm⁻¹ was detected by FTIR

Figure 1 Characterizations of phosphorene-H. (a) Side view of optimized structures of phosphorene and phosphorene-H obtained from DFT calculations. The purple and white balls represent phosphorus and hydrogen atoms, respectively. (b) Top view of atomic configuration model of phosphorene along the [010] orientation. The purple balls symbolize phosphorus atoms. Top view of HAADF-STEM images of (c) phosphorene and (d) phosphorene-H along the [010] orientation (insets: lattice distances of (200) facets based on the intensity line profiles). Normalized *in-situ* Raman mapping of (e) phosphorene and (f) phosphorene-H. The intensity of A_g^1 mode was considered for the mapping, normalized by the intensity of the Si transverse optical mode. The samples were prepared by drop-casting the suspension onto a Si/SiO₂ substrate.

spectroscopy (Fig. S3) [35], which further manifested the formation of P–H covalent bonds in phosphorene-H. Notably, hydrogenation treatment can significantly reduce the unavoidable oxides on the surface of phosphorene-H based on the XPS results (Fig. S4). The atomic ratio of P:H in phosphorene-H was estimated to be 1:0.05 by elemental analysis. In order to rule out the formation of P vacancies in phosphorene-H, we detected whether PH₃ was generated during the hydrogenation process of phosphorene. Typically, an aqueous CuSO₄ solution was used to adsorb the exhaust gas during the hydrogenation process. However, Cu_xP_y species were not detected from XRD and inductively coupled plasma (ICP) results until the end of the hydrogenation reaction. These results revealed that P vacancies were not generated during this hydrogenation process. Further, based on careful discrimination of the phosphorene-H atomic phase along the [010] orientation (Fig. 1d), vacancy defects were not observed in the phosphorene-H after hydrogenation treatment. Therefore, we believe that P vacancies were not formed in phosphorene-H.

In order to further confirm the P–H covalent bond characteristics, Raman spectroscopic measurements and XRD were conducted. As illustrated in Fig. S5, the intensity of the three Raman bands of phosphorene decreased by a certain extent after hydrogenation treatment. Based upon previous reports on aryl diazonium covalent modification of phosphorene [22], the

decrease in the Raman band intensity has been attributed to the formation of a P–H covalent bond. Subsequently, *in-situ* Raman mapping was taken on one single nanosheet, and the A_g^1 mode intensity was considered for mapping, which remained constant when normalized to the Si transverse optical mode [36]. In a constant crystallographic orientation, the Raman intensity of the A_g^1 mode of phosphorene-H decreases except for the edge of the nanosheet compared with phosphorene (Fig. 1e, f), suggesting that the phosphorene surface possesses an appropriate covalent affinity for the H atom. Furthermore, XRD patterns also confirm this speculation. As shown in Fig. S6, a close inspection of the (020), (040), and (060) diffraction peaks reveals that the phosphorene-H peak positions shift slightly toward a lower 2θ value compared with that of phosphorene. The lowered diffraction angles suggest an increased lattice distance of the (020) facet (5.23 Å) which is 0.4% larger than that of phosphorene (5.21 Å) due to the formation of P–H covalent bonds on the (020) facet. Collectively, the experimental results of XRD, *in-situ* Raman mapping, FTIR spectroscopy, HAADF-STEM images, and DFT calculations converge to provide compelling evidence for the formation of P–H covalent bonds on the (020) facet of phosphorene-H.

Stability evaluation of phosphorene-H

It is believed that oxygen and water cause phosphorene degra-

dation in an ambient environment, and illumination is not necessary but can accelerate the degradation rate of phosphorene [11]. In our study, the degradation behavior of samples was explored in two different environments: (i) in water (temperature: $25 \pm 3^\circ\text{C}$, ambient light); (ii) in ambient air (temperature: $25 \pm 3^\circ\text{C}$, relative humidity: $80 \pm 5\%$, ambient light). The samples kept in water and ambient air were examined with UV-vis absorption spectroscopy and AFM, respectively, to monitor the degradation process. The concentration of freshly prepared phosphorene and phosphorene-H suspension in water is 25.4 and 26.9 mg L^{-1} , respectively (Fig. S7). For phosphorene, the intensity of UV-vis absorption decreased sharply with increasing storage time (Fig. 2a). After being maintained in water for 18 days, the proportion of the degraded phosphorene reached 72 mol%, and the suspension color changed from brown to almost colorless (Fig. S8a). Previous studies have established that in the course of degradation, phosphorene is easily oxidized and dissolved in water in the form of PO_x^{3-} , which is optically transparent in the region of 300–800 nm [11]. In comparison, the phosphorene-H suspension was essentially unchanged and still existed in the colloidal form in water after being maintained under the same testing conditions for 18 days (Fig. S8b). Based

on the intensity changes of UV-vis absorption in phosphorene-H, the corresponding degradation fraction was determined to be only 7 mol% (Fig. 2b).

AFM measurements also probed the stability of the samples in ambient air. As shown in Fig. 2c, f, the thickness of phosphorene and phosphorene-H is $\sim 1.5 \text{ nm}$, corresponding to approximately 3 atomic layers. With regard to phosphorene, small holes could be seen shortly after exposure to ambient air. After 7 days, the holes became larger and denser (Fig. 2d). An exposure time of 15 days led to a further increase in the hole size and possible fusion. As a result, some phosphorene parts vanished (Fig. 2e). Generally, bubbles often appear on the phosphorene surface due to the formation of P_xO_y through the reaction between O_2 and phosphorene [7,15,18]. However, in our research, P_xO_y may be dissolved and removed from the surface utilizing water vapor due to the high relative humidity, which leads to the appearance of holes [19]. In contrast, phosphorene-H functionalized with P–H covalent bonds exhibits markedly improved morphological stability. After 7 days of exposure in experimental conditions, the nanosheet morphology remains intact with no discernible sign of degradation (Fig. 2g). Only a small hole appeared on the surface of phosphorene-H after 15 days of exposure (Fig. 2h).

Figure 2 Stability evaluation of phosphorene and phosphorene-H. Evolution of UV-vis absorption spectra of (a) phosphorene and (b) phosphorene-H suspensions kept in water. Evolution of morphologies and the corresponding height profiles of phosphorene maintained in ambient air for (c) 2 h, (d) 7 days, and (e) 15 days. Evolution of morphologies and the corresponding height profiles of phosphorene-H kept in ambient air for (f) 2 h, (g) 7 days, and (h) 15 days.

Therefore, the combined UV-vis and AFM studies reveal that the chemical stability of phosphorene-H against water and ambient air has been substantially improved under the formation of P-H covalent bonds.

Stability mechanism of phosphorene-H

Phosphorene oxidation has been initiated by dissociating the O₂ molecule adsorbed on the phosphorene surface [11,37,38]. The lone pairs of phosphorene induce elongation of the O-O bond length of O₂. Then, a slight energy fluctuation can break the O-O bond and lead to the oxidation of phosphorene. In contrast to phosphorene, the phosphorene-H lone pairs are passivated to some extent due to the existence of a P-H covalent bond, thus delaying the adsorption and activation of the O₂ molecule. In the following, DFT calculations based on the corresponding reaction coordinate were carried out to simulate this conjecture. As shown in Fig. 3b, the P-O distance between O₂ and the phosphorene-H surface is slightly longer than that of phosphorene in the initial state (IS), implying a weaker interaction between O₂ and phosphorene-H. Thus, compared with phosphorene's energy barrier (0.13 eV) in the transition state (TS), more energy is required to overcome an energy barrier of 0.21 eV for phosphorene-H (Fig. 3a), suggesting that phosphorene-H is more chemically stable to O₂ than phosphorene in terms of kinetics. Moreover, the final state (FS) *via* the reaction path of phosphorene-H is about 0.7 eV higher than that of phosphorene (Fig. 3a), signifying that the oxidation reaction of phosphorene-H is hindered thermodynamically. In addition, to discern the influence of P-H covalent bonds on photocatalytic performance, the effective masses of electrons along the [100] and [001] orientations were estimated by DFT calculations, considering the anisotropic characteristics of the phosphorene structure. It is well known that the effective mass of electrons significantly

impacts the ability to transfer the carrier to the surface reactive site, which plays a vital role in photocatalytic activity [39–41]. As shown in Fig. S9 and Table S1, the electron effective mass of phosphorene-H is roughly the same as that of phosphorene along the [100] and [001] orientations, meaning that electron transfer to the reactive sites on the phosphorene-H surface is not affected by the P-H covalent bond. Therefore, introducing P-H covalent bonds provides phosphorene-H with improved stability compared with phosphorene while retaining its photocatalytic performance.

Photocatalytic durability evaluation of phosphorene-H

Inspired by the above results, we examined the durability of phosphorene-H for photocatalytic H₂ evolution. Each cycle experiment includes 3 h of photocatalysis evaluation and 20 h of exposure to ambient air. As shown in Fig. 4a, the freshly prepared phosphorene suspension displayed a H₂ evolution rate of 340 $\mu\text{mol g}^{-1} \text{h}^{-1}$, corresponding to a production of 1.02 μmol H₂ in 3 h. However, its photocatalytic activity dropped sharply and only retained 30% of its initial activity during the third cycle, which could be ascribed to the oxidative degradation in ambient air. In sharp contrast, the photocatalytic activity of the freshly prepared phosphorene-H only slightly decreased owing to shrinkage of the active surface area, but its performance remained stable after 10 cycles (Fig. 4b). The amount of H₂ produced during the first, fifth, and tenth cycles is 0.92, 0.89, and 0.84 μmol , respectively. As a result, introducing P-H covalent bonds is an effective protection strategy for exploiting phosphorene in photocatalysis. A series of controlled experiments aiming at gaining a better understanding of the photocatalytic process were performed. It was found that the photocatalyst (phosphorene-H), sacrificial agent (methanol), and light were all essential for successful H₂ evolution (Fig. S10). The absence of

Figure 3 Stability mechanism of phosphorene-H. (a) Reaction coordinates for O₂ dissociation on the surface of phosphorene and phosphorene-H obtained using DFT calculations. (b) Optimized structures of phosphorene and phosphorene-H corresponding to IS, TS, and FS. The purple, white, and red balls represent phosphorus, hydrogen, and oxygen atoms, respectively.

Figure 4 Photocatalytic durability evaluation. Durability test of photocatalytic H₂ evolution for (a) phosphorene and (b) phosphorene-H.

any components resulted in no H_2 evolution, suggesting a photo-driven catalytic process. Finally, a series of characterizations were performed on recovered photocatalyst phosphorene-H. The XRD patterns, Raman, and FTIR results of the recovered phosphorene-H are consistent with those of the as-prepared sample (Figs S11–S13). Moreover, the XPS spectrum of the recovered sample demonstrates a slight increase in the oxygen content (Fig. S14b), likely due to the chemical adsorption of H_2O molecules on the phosphorene-H surface. Collectively, the above data further support the excellent catalytic stability of phosphorene-H.

CONCLUSIONS

We have demonstrated that introducing P–H covalent bonds can strengthen the stability of phosphorene-H in ambient air and water. Experimental and DFT calculation studies unveil that the presence of P–H covalent bonds hinders the reaction between O_2 and phosphorene-H in terms of thermodynamics and kinetics, thus mitigating the oxidation of phosphorene-H. In the meantime, this surface functionalization approach allows phosphorene-H to preserve the high carrier mobility and photocatalytic H_2 evolution activity. The present study provides a pathway to construct stable and efficient photocatalytic systems based on phosphorene-H and stimulates further investigation on their applications in other fields.

Received 18 August 2021; accepted 25 October 2021;
published online 9 December 2021

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Acknowledgements We thank the financial support from the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17000000) and the National Natural Science Foundation of China (21773275 and 21971250). Chen Y acknowledges the financial support from K.C. Wong Education Foundation and the CAS-Croucher Funding Scheme for Joint Laboratories.

Author contributions Shi R conducted most of the experiments and wrote the manuscript; Kang L carried out theoretical calculations; Bai X participated in the discussion and analysis; Chen Y conceived and supervised the project.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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通过 P-H 键对磷烯进行表面功能化以提升磷烯的稳定性并实现高效光催化产 H_2

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摘要 在大气环境下, 寡层黑磷(简称为磷烯)很容易被氧化, 因此阻碍了其在光催化太阳能转换领域的应用. 相关的一些保护方法, 比如在磷烯表面引入保护层、表面配位、P-C共价官能化等方法可以维持磷烯的稳定性, 使其免受氧化降解, 可是这些方法对磷烯的催化活性位点造成了堵塞, 因此不可避免地降低了其光催化活性. 在本项工作中, 我们开发了一种在磷烯表面引入 P-H 共价键的策略, 表面P-H 共价键的引入既能维持磷烯在大气环境下的稳定性, 又能实现高效光催化分解水产 H_2 . 相关实验和 DFT 计算表明, 磷烯表面约5 mol% 的磷原子参与了 P-H 共价键的形成, 在热力学和动力学两方面同时抑制了磷烯的氧化反应. 磷烯的表面氢化策略有望促进磷烯在光催化领域的实际应用.