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Ab initio Study of Hydrogen Adsorption on Metal-Decorated Borophene-Graphene Bilayer

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Abstract: We studied the hydrogen adsorption on the surface of a covalently bonded bilayer borophene-graphene heterostructure decorated with Pt, Ni, Ag, and Cu atoms. Due to its structure, the borophene-graphene bilayer combines borophene activity with the mechanical stability of graphene. Based on the density functional theory calculations, we determined the energies and preferred adsorption sites of these metal atoms on the heterostructure’s borophene surface. Since boron atoms in different positions can have different reactivities with respect to metal atoms, we considered seven possible adsorption positions. According to our calculations, all three metals adsorb in the top position above the boron atom and demonstrate catalytic activity. Among the metals considered, copper had the best characteristics. Copper-decorated heterostructure possesses a feasible near-zero overpotential for hydrogen evolution reaction. However, the borophene-graphene bilayer decorated with copper is unstable with respect to compression. Small deformations lead to irreversible structural changes in the system. Thus, compression cannot be used as an effective mechanism for additional potential reduction.

Keywords: hydrogen evolution reaction; borophene; graphene; single-atom catalyst; density functional theory

1. Introduction

Fossil fuels are currently a major source of energy. However, this situation will change in the coming decades. Firstly, fossil fuel reserves are limited. Secondly, the combustion of hydrocarbons leads to the release of CO₂ and other gases that create a greenhouse effect and negatively affect the biosphere. Hydrogen energy is considered an attractive alternative to traditional fossil fuels. The hydrogen reserves are huge, and the result of its oxidation is water, an environmentally friendly substance. Therefore, the efforts of researchers around the world are aimed at finding effective ways to produce, store, and use hydrogen. The current technologies do not ensure the competitiveness of hydrogen energy in most applications. However, improving these technologies will help change this situation.

Electrocatalytic water splitting is one of the most developed hydrogen-producing methods [1]. Hydrogen evolution reaction (HER) is one of the key points of this technology. Therefore, the improvement of catalysts for HER is of special interest [1]. Traditional catalysts based on platinum and other noble metals have a high cost, so researchers...
are looking for alternative solutions. The use of metal nanoparticles can significantly reduce the required amount of noble metal and reduce the cost of releasing energy [2]. However, even in a nanoparticle, only a small fraction of the atoms are on the surface and participate in catalysis. Therefore, another approach, known as single-atom catalysis (SAC), is actively developed [3–5]. This approach implies that HER conducts on a single metal atom rather than on the surface of nanoparticles. Due to their huge specific surface area and strong interaction with metals, 2D materials are excellent substrates for individual metal atoms. The concentration of metal atoms on the surface of a 2D material can be easily controlled [6]. For example, vanadium, rhodium, and iridium atoms adsorbed on nitrogen-doped graphene were predicted to be the efficient catalysts for HER [7]. Cobalt atoms, trapped in nitrogen-doped graphene and forming planar pseudo-square coordination structures, also demonstrates high catalytic activity to HER [8]. Borophene decorated with different transition metal atoms provides good kinetic for both HER and oxygen evolution reactions [9]. In addition, Co atoms on borophene were predicted to be useful for the reduction of carbon dioxide [10]. The 2D-MoS\(_2\) monolayer is a suitable substrate for Ni and Co atoms, which provided high-performing HER [10]. For the same purposes, silicene decorated with Ti, V, Mn, Fe, and Co atoms was considered [11]. Therefore, the “2D material + metal atoms” structures are quite common SAC systems for HER. Moreover, the catalytic activity of such systems can be tuned via simultaneous adsorption of atoms of different metals [12] and through the curvature [13] or stretching [14] of 2D substrates.

The interaction of metal atoms with 2D substrate defines their catalytic properties. The structure, defects, and mechanical properties of the underlying 2D material play an important role in HER catalysts. This is why novel 2D materials, such as phosphorus carbide [15–17] or stanene [18,19], are considered for catalytic applications. As an alternative to single-layer 2D materials, researchers consider heterostructures constructing two or more different monolayers. In particular, bilayer structures consisted of graphene and another 2D material are considered. In such structures, graphene’s exceptional mechanical properties [20] and the ability to modify its properties via strain [21] can be supplemented by specific features of another material. The Van-der-Waals heterostructures of graphene with other sheets are quite common. For example, graphene/h-BN [22], graphene/phosphorene [23], graphene/silicene [24], graphene/MoS\(_2\) [25], and graphene/stanene [26] were synthesized and used in various applications. Another innovation is covalently bonded bilayer structures, in which covalent bonds are formed between two layers. In 2019, Liu and Hersam grew a covalently bonded borophene-graphene heterostructure on Ag(111) substrate [27]. Interlayer bonds result in distortion of electronic structures and properties of both sheets. The final borophene-graphene heterostructure possesses metallic properties, but a band gap can be opened via the mechanical strain [28]. This novel heterostructure has the highest 2D Young’s modulus among all other 2D materials [28]. A similar borophene-graphene structure was used as a basis of the humidity sensor, which demonstrated the highest sensitivity among all the reported chemiresistive sensors based on 2D materials [29]. It also kept high stability under bending [29]. Exceptional mechanical characteristics of borophene-graphene heterostructures explain growing research interest to them.

This paper considers the HER reaction’s efficiency on a bilayer borophene-graphene heterostructure decorated with individual metal atoms. Along with the traditional catalytic metal, platinum, we investigated cheaper metals, silver, and copper. The choice of these metals is explained by the fact that they have demonstrated their excellent electrocatalytic properties on the surface of pure \(\alpha\)-borophene [9].

2. Materials and Methods

2.1. Atomistic Model of the Borophene-Graphene Heterostructure

The graphene-borophene heterostructure was represented as a hexagonal unit cell \(\text{C}_{32}\text{B}_{48}\) in the form of a rhombus with a side of \(\approx 1\) nm (see Figure 1). The striped borophene and graphene layers were connected by sixteen interlayer covalent B-C bonds in each unit
cell. Periodic boundary conditions were applied in all directions. A period along the z-axis was chosen to be 5 nm to preserve any interaction. Adsorption of metal atoms disturbs the hexagonal symmetry of the system. Therefore, both in-plane translational vectors and their angle were optimized together with the atomic positions without any symmetry constraints. Optimized geometry of this structure is available in Supplementary materials Tables S1.

2.2. Details of the Density Functional Calculations

Density functional theory calculations were performed with the QUANTUM ESPRESSO version 6.7 software [30,31]. We used projector-augmented wave pseudopotentials [32,33] with the kinetic energy cutoff for wavefunctions of 60 and 90 Ry. A Monkhorst-Pack k-point grid [34] of 4 × 4 × 1 and 8 × 8 × 1 combined with the first-order Methfessel-Paxton scheme [35] with a smearing of 0.01 Ry were applied. In all cases, the total energies and energy differences calculated with the higher and lower values of the cutoff energy and k-point grid were below 1%. This fact indicates that the chosen parameters are sufficient for convergence. Grimme’s dispersion corrections D2 [36] were added to reproduce the non-covalent interaction of heterostructure with metal atoms. Structural optimizations were continued until residual forces become smaller than 0.1 meV/Å.

The adsorption energies of metal atoms $E_m$ on the heterostructure were calculated as

$$E_m = E(\text{C}_{32}\text{B}_{48}) + E(\text{M}) - E(\text{C}_{32}\text{B}_{48}\text{M}),$$  

(1)

where $E(\text{C}_{32}\text{B}_{48})$, $E(\text{M})$, and $E(\text{C}_{32}\text{B}_{48}\text{M})$ are total energies of the pristine unit cell, metal atom, and metal-decorated unit cell, respectively; M = Pt, Ni, Cu, Ag. In this determination, strong bonding between the substrate and the adsorbed metal atom corresponds to a large positive value of $E_m$. The adsorption energy of hydrogen atom $E_H$ was calculated with a similar formula:

$$E_H = E(\text{C}_{32}\text{B}_{48}\text{M}) + 0.5E(\text{H}_2) - E(\text{C}_{32}\text{B}_{48}\text{MH}).$$  

(2)

here $E(\text{H}_2)$ and $E(\text{C}_{32}\text{B}_{48}\text{MH})$ are the total energies of the hydrogen molecule and the metal-decorated unit cell with one adsorbed hydrogen atom, respectively. Finally, the overpotential $\eta$ of HER on the heterostructure surface was estimated as [17]

$$\eta = -E_H - 0.29 \text{ eV} \left/ e, \right.$$  

(3)

where $e$ is the elementary charge. The value 0.29 eV takes into account all required corrections to get an adequate value of the Gibbs energy changing during the HER.

Figure 1. Atomistic model of the borophene-graphene bilayer. Green and brown balls represent boron and carbon atoms, respectively.
3. Results and Discussion

3.1. Interaction of Metals Atoms with the Borophene-Graphene Bilayer

There are two types of interaction of metal atoms with 2D materials. In the first case, the metal atom is embedded in the sheet’s lattice, replacing the carbon or boron atom. In the second case, the metal atom is adsorbed over the sheet’s surface, preserving the substrate’s original structure. In the present study, we limited ourselves to the latter type of adsorption and investigated the so-called “metal-decorated” sheets. They exhibit higher mechanical strength due to the undistorted crystal lattice.

Among the decorating metals under consideration (Pt, Ni, Cu, Ag), only the platinum atom rather strongly interacts with graphene (the adsorption energy is about 2 eV [37]). Simultaneously, the copper atom induces structural defects in graphene [38] and is only used when embedded in the lattice [39]. As for the decorating silver atom, it interacts weakly with graphene [40]. So, we used the more active borophene side for the loading of metal atoms. As known, pure borophene strongly interacts with metal atoms. Thus, we studied the underlying graphene effect on such interactions.

In contrast to pure borophene, the considered borophene-graphene structure has three inequivalent positions for boron atoms, as shown in Figure 2. Atoms at the first position are bound with carbon atoms (labeled as red in Figure 2). Atoms at the second positions are placed above carbon atoms but are not bonded with them (labeled as green in Figure 2). Finally, atoms at the third position are placed above the graphene’s hexagonal hole (labeled as beige in Figure 2). Boron atoms in different positions can possess different reactivity toward metal atoms. Therefore, we considered seven adsorption positions, labeled as 1 ÷ 7 in Figure 2. The first three are the atop positions firmly above the boron atoms, four and seven are the bridged positions above the center of covalent bonds, whereas five and six are two different hole positions. Corresponding adsorption energies and bond lengths for different adsorption positions are listed in Table 1. The data in Table 1 shows that all three atoms are strongly bound to the surface of the structure. Position number two above the boron atom is the most energetically favorable. This is due to the fact that the atoms in the second position are slightly elevated above the rest of the boron atoms. Since the second position provides much higher adsorption energies, we shall consider this position further. In addition, bond lengths between boron and metal atoms in position number two are about 2 Å. This fact additionally indicates strong binding. Optimized geometries of the Cu- and Ag-decorated structures are available in Supplementary Materials: Tables S2 and S3, respectively.

![Figure 2. Different adsorption positions for metal atoms on the borophene side of the borophene-graphene bilayer structure are numbered as 1 ÷ 7. Brown atoms and bonds represent underlying graphene. Red, green, and beige balls represent boron atoms in different non-equivalent positions.](image-url)
3.2. Interaction of Hydrogen Atom with the Metal-Decorated Borophene-Graphene Bilayer

Figure 3 shows a hydrogen atom adsorbed on the metal-decorated borophene-graphene bilayer. We observed such configurations for the Cu- and Ag-decorated structures. As to the Pt- and Ni- decorated structures, it lost its stability as a result of hydrogen adsorption. These atoms were embedded in the borophene lattice, creating irreversible defects. Such behavior is explained by the strong interaction between the platinum or nickel atoms and the two-layer sheet, as can be seen from the data in Table 1. Therefore, we excluded platinum and nickel from further consideration. Data concerning Cu and Ag atoms are presented in Table 2. One can see that the Cu-decorated system provides quite feasible HER overpotential close to zero. Note that the $E_H$ value for the H atom adsorption on the bare borophene surface of the considered structure without decorated metals is equal to $-1.19$ eV, and the corresponding $I_{B-H}$ bond is equal to 1.183 Å. So decorating metals atoms are facilitated HER significantly. Optimized geometries of the Cu- and Ag-decorated structures with adsorbed hydrogen atom are available in Supplementary Materials: Tables S4 and S5, respectively.

![Figure 3](image-url)

Figure 3. Adsorption of the hydrogen atom on the metal-decorated borophene-graphene structure. Brown, green, blue, and white balls represent carbon, boron, metal, and hydrogen atoms, respectively.

Table 1. Adsorption energies (see Equation (1)) for metal atoms Cu, Ag, Pt, and Ni adsorbed on different sites (see Figure 2) of the borophene-graphene bilayer. Ranges of bond lengths between metal and boron atoms are also presented. Record “to N” indicates that the metal atom moved to position number N during geometry optimization.

| Position | 1     | 2     | 3     | 4     | 5     | 6     | 7     |
|----------|-------|-------|-------|-------|-------|-------|-------|
| $E_{Cu}$ (eV) | 2.51  | 3.05  | 2.35  | to 3  | to 3  | to 1  | to 3  |
| $l_{B-Cu}$ (Å) | 2.138 ÷ 2.219 | 2.142 | 2.174 | -     | -     | -     | -     |
| $E_{Ag}$ (eV) | 1.42  | 1.98  | 1.55  | 1.53  | 1.55  | 1.55  | to 2  |
| $l_{B-Ag}$ (Å) | 2.468 ÷ 2.616 | 2.045 | 2.471 ÷ 2.474 | 2.220 ÷ 2.356 | 2.310 ÷ 2.371 | -     | 2.310 ÷ 2.371 |
| $E_{Pt}$ (eV) | to 2  | 5.93  | to 2  | to 2  | to 2  | to 2  | to 2  |
| $l_{B-Pt}$ (Å) | -     | 2.093 | -     | -     | -     | -     | -     |
| $E_{Ni}$ (eV) | to 2  | 4.84  | to 2  | to 2  | to 2  | to 2  | to 2  |
| $l_{B-Ni}$ (Å) | -     | 2.002 | -     | -     | -     | -     | -     |

Table 2. Adsorption energies $E_H$ (see Equation (2)) of the hydrogen atom on the Cu- and Ag-decorated borophene-graphene bilayer structures. Metal-hydrogen bond lengths between and HER overpotentials $\eta$ (see Equation (3)) and total Löwdin charges of metal and hydrogen atoms are also presented.

| Metal | $E_H$ (eV) | $l_{M-H}$ (Å) | $\eta$ (V) | $q_M$ (e) | $q_H$ (e) |
|-------|------------|---------------|----------|----------|----------|
| Cu    | 0.01       | 1.528         | -0.28    | 10.89    | 1.17     |
| Ag    | -0.35      | 1.651         | -0.64    | 10.84    | 1.16     |
3.3. Effect of Mechanical Strain of Cu-Decorated Borophene-Graphene Bilayer on HER Overpotential Value

For the further tuning of HER overpotential, we applied a mechanical strain to the Cu-decorated bilayer structure. It is well-known that the strain of 2D materials can change their interaction with hydrogen atoms (see, for example, Ref. [41] for graphene, Ref. [17] for metal-doped borophene, Ref. [42] for graphene/silicene, or Ref. [43] for the novel BPC structure). We considered biaxial deformation because it can be easier implemented experimentally. The effect of uniaxial deformation depends on the crystallographic direction in which it is applied. Thus, in order to achieve the desired effect, the structure should be controllably oriented. This creates additional technical difficulties, especially when it comes to a polycrystalline sample or an array of nanostructures. So we applied biaxial hydrostatic deformation $\varepsilon$ to the Cu-decorated borophene-graphene bilayer system. Under the strain of 1.05, we observed a decrease in the $E_H$ value to $-0.52$ eV, which corresponds to a change in the overpotential $\eta$ to $-0.81$ V. Such a behavior is explained by the stronger bond of the stretched substrate with the copper atom, which leads to a weakening of the copper-hydrogen bond. This bond elongates by 0.004 Å as a result of stretching. Therefore, to reduce the absolute value of the overpotential $\eta$, one needs to compress the structure.

Note that the compression of 2D materials leads to their rippling rather than to the shortening of interatomic bonds [44]. However, our calculations showed that the Cu-decorated borophene-graphene structure is unstable with respect to compression. Deformation of 0.95 and even 0.98 led to irreversible structural changes of the system, which is associated with the weakening of the bonds between borophene and graphene in the presence of a copper atom. Thus, the compression cannot be applied as an effective mechanism for the additional reduction of the potential.

4. Conclusions

In summary, we investigated the catalytic properties of individual metal atoms on the surface of the borophene-graphene bilayer. Due to its structure, this bilayer combines the activity of borophene with the mechanical stability of graphene. We found that the copper atom can serve as an effective catalyst center for HER. However, the mechanical properties of the structure restrict the ability for further tuning of catalytic properties by mechanical compression.

The presented study is an example of the utility of a bilayer sheet with covalently bound layers. Such 2D sheets differ significantly in properties from traditional Van der Waals heterostructures. We believe that such structures with covalently bound layers will breathe new life into the physics and technology of 2D materials. In particular, they can demonstrate their power for the single-atom catalysis of HER reaction.

Supplementary Materials: The optimized geometries of the considered borophene-graphene structures decorated with metal atoms in the most feasible position are available online at https://www.mdpi.com/article/10.3390/en14092473/s1, Table S1: pristine borophene-graphene structure, Table S2: Cu-decorated borophene-graphene structure, Table S3: Ag-decorated borophene-graphene structure, Table S4: hydrogenated Cu-decorated borophene-graphene structure, Table S5: hydrogenated Ag-decorated borophene-graphene structure.

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30. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G.L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J. Phys. Cond. Matt.* 2009, 21, 395502. [CrossRef]

31. Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Nardelli, M.B.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys. Cond. Matt.* 2017, 29, 465901. [CrossRef]

32. Blöchl, P.E. Projector augmented-wave method. *Phys. Rev. B* 1994, 50, 17953–17979. [CrossRef]

33. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 1999, 59, 1758–1775. [CrossRef]

34. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* 1976, 13, 5188–5192. [CrossRef]

35. Methfessel, M.; Paxton, A.T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* 1989, 40, 3616–3621. [CrossRef] [PubMed]

36. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comp. Chem.* 2006, 27, 1787–1799. [CrossRef] [PubMed]

37. Wella, S.A.; Hamamoto, Y.; Morikawa, Y.; Hamada, I. Platinum single-atom adsorption on graphene: A density functional theory study. *Nanoscale Adv.* 2019, 1, 1165–1174. [CrossRef]

38. Kano, E.; Hashimoto, A.; Kaneko, T.; Tajima, N.; Ohno, T.; Takeguchi, M. Interactions between C and Cu atoms in single-layer graphene: Direct observation and modelling. *Nanoscale* 2016, 8, 529–535. [CrossRef] [PubMed]

39. Han, G.; Zheng, Y.; Zhang, X.; Wang, Z.; Gong, Y.; Du, C.; Banis, M.N.; Yiu, Y.M.; Sham, T.K.; Gu, L.; et al. High loading single-atom Cu dispersed on graphene for efficient oxygen reduction reaction. *Nano Energy* 2019, 66, 104088. [CrossRef]

40. Galashev, A.Y.; Katin, K.P.; Maslov, M.M. Morse parameters for the interaction of metals with graphene and silicene. *Phys. Lett. A* 2019, 383, 252–258. [CrossRef]

41. Katin, K.P.; Prudkovskiy, V.S.; Maslov, M.M. Chemisorption of hydrogen atoms and hydroxyl groups on stretched graphene: A coupled QM/QM study. *Phys. Lett. A* 2017, 381, 2686–2690. [CrossRef]

42. Kistanov, A.A.; Cai, Y.; Zhang, Y.W.; Dmitriev, S.V.; Zhou, K. Strain and water effects on the electronic structure and chemical activity of in-plane graphene/silicene heterostructure. *J. Phys. Condens. Matter* 2017, 29, 095302. [CrossRef] [PubMed]

43. Kistanov, A.A.; Shcherbinin, S.A.; Ustiuzhanina, S.V.; Huttula, M.; Cao, W.; Nikitenko, V.R.; Prezhdo, O.V. First-Principles Prediction of Two-Dimensional B3C2P3 and B2C4P2: Structural Stability, Fundamental Properties, and Renewable Energy Applications. *J. Phys. Chem. Lett.* 2021, 12, 3436–3442. [CrossRef] [PubMed]

44. Baimova, J.A.; Korznikova, E.A.; Dmitriev, S.V.; Liu, B.; Zhou, K. Wrinkles and wrinklons in graphene and graphene nanoribbons under strain. *Curr. Nanosci.* 2016, 12, 184–191. [CrossRef]