

# Stability and electronic structure of iron nanoparticle anchored on defective hexagonal boron nitrogen nanosheet: A first-principle study



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## ABSTRACT

By first-principle methods, we investigate the stability and electronic structures of Fe<sub>13</sub> nanoparticles anchored on hexagonal boron nitrogen nanosheets (h-BNNSs) with monovacancy defect sites. It is found that the defect sites such as boron and nitrogen vacancy significantly increase the adsorption energies of Fe<sub>13</sub>, suggesting that the supported Fe<sub>13</sub> nanoparticles should be very stable against sintering at high temperatures. From the calculated density of states, we testify that the strong interaction is attributed to the coupling between the 3d orbitals of Fe atoms with the sp<sup>2</sup> dangling bonds at the defect sites. The Bader charge and differential charge density analyses reveal that there is significant charge redistribution at the interface between Fe<sub>13</sub> and the substrates, leading to positive charges located on most of the Fe atoms. Additionally, our results show that the strong binding of the nanoparticle results in the upshift of d-band center of Fe<sub>13</sub> toward the Fermi level, thus making the surface Fe atoms with higher reactivity. This work gives a detailed understanding the interaction between Fe<sub>13</sub> nanoparticle and defective h-BNNS and will provide helpful instructions in the design and synthesis of supported Fe-based catalysts in heterogeneous catalysis.

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## 1. Introduction

Metal nanoparticles anchored on graphene can further tune their catalytic properties by surface-nanoparticle electron transform. Due to the potential applications, the graphene supported metal nanoparticles have attracted increasing attention both experimentally and theoretically [1–12]. In particular, the available defect sites play a vital role in making graphene as an ideal substrate for growth of nanoparticles for high-performance catalysts and other electrochemical devices [5–8,13–15]. For example, a previous experimental report finds that the defects on graphene substrates allow for the controlled morphology of iron nanoparticles, enhancing the rate of electron transport [15]. Recent theoretical studies suggest that metal (such as Pt, Pd, Ru, and Fe) nanoparticles embedded in graphene with vacancies exhibit high catalytic activity [5,6,8–12,14]. These studies indicate a possible new direction in designing future catalysts with high efficiency and also motivate people to exploit the other novel two-dimensional materials for the anchoring of metal nanoparticles.

In the past few years, hexagonal boron nitrogen (h-BN), has attracted considerable attention for various applications mainly due to their superb thermal stability, high thermal conductivity, and high electrical resistance [16–22]. Although the defect-free h-BN nanosheet (h-BNNS) is probably too stable to influence the physical and chemical properties of deposited metal atoms and clusters, h-BNNSs, particularly those with the boron and nitrogen vacancies, share many characteristics with graphene and might be used to create novel composites through the anchoring of guest metals in their defect sites. Importantly, being superior to graphene-based materials which are observed to burn at temperatures below 800 K, h-BNNSs can remain stable at much higher temperatures, up to 1000 K [23,24].

As indicated in the theoretical studies by us and the other groups, the defective h-BNNSs are capable of anchoring metal atoms such as Ru, Cu, Ag, Au, Pt, Rh, Pd, Fe, Co and these nanocomposites have considerable reactivity for CO oxidation [25–27]. On the other hand, the metal nanoparticles with a size of less than 10 nm have attracted a great deal of attention due to their applications in magnetism, electronics, and catalysts [28–31]. Accordingly, it is inspired that the interaction between metal nanoparticle and defective h-BNNS might not only help to stabilize the fine dispersion of the metal catalysts so as to avoid sintering but also dramatically influence the shape, size, electronic structure and catalytic activity of the metal catalysts.

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Despite a number of studies have been devoted to elucidate such an interaction as well as its effect on the activity of catalytic reactions, some key issues such as the configuration of the metal-support interface and the electronic structures of the supported metal nanoparticles are still not fully understood due to the limitation of experimental techniques. In order to design novel and high-performance catalysts, it is highly desirable to obtain a detailed understanding of the interaction between metal nanoparticles and defective h-BNNSs.

In this present work, iron is chosen as the metal catalyst since it is inexpensive, environmentally friendly, and rich in the earth, almost meeting the requirements to develop low-cost green catalysts. More importantly, iron catalysts have been widely used in heterogeneous catalysis, owing to their high activity and/or selectivity in many industrially important catalytic processes [32–36]. For example, iron nanoparticles with different cluster size exhibit catalytic activity for  $\text{NH}_3$  decomposition [32,33], which can lead to the  $\text{CO}_x$ -free hydrogen production. After supported by defective graphene, Fe nanoparticles are theoretically presumed to exhibit superior catalytic performance in the low-temperature catalytic dehydrogenation of  $\text{NH}_3$  due to a shift of d-band center [37]. Another important application is the direct CO dissociation on iron metals [34–36]. Because of being an important first step and often the rate-determining step followed by hydrogenation of chemisorbed carbon to form  $\text{CH}_x$  ( $x=1-3$ ) monomers in Fischer–Tropsch synthesis, it has attracted increasing attention from academic researchers and for industrial applications.

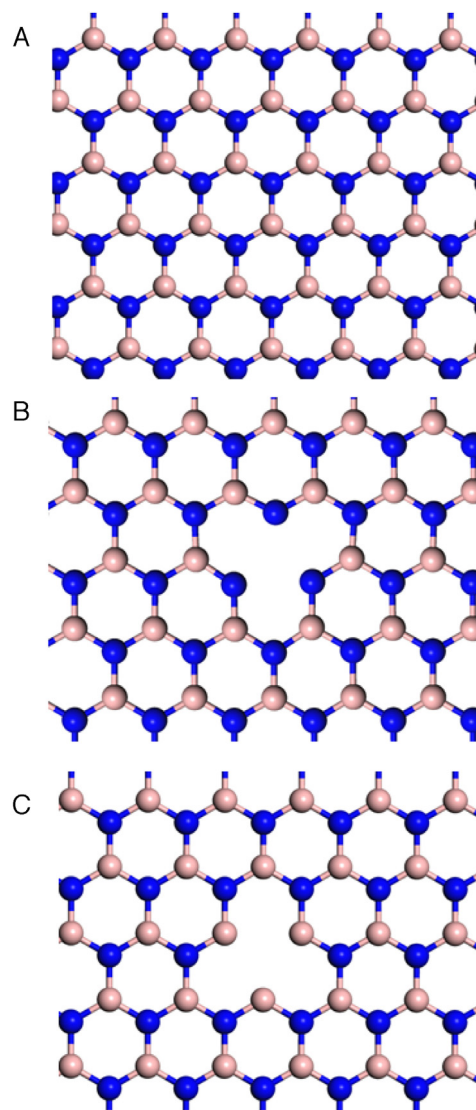
Based on the above discussion, the defective h-BNNS substrate may enhance the stability and improve the catalytic properties of iron metal nanocatalysts. To confirm these two points, we explore the interaction between  $\text{Fe}_{13}$  nanoparticle and defective h-BNNS by means of periodic first-principle methods. Our studies mainly focus on the energetic stability and electronic properties of the supported  $\text{Fe}_{13}$  ( $\text{Fe}_{13}/\text{BNNS}$ ). This work provides a detailed understanding on the  $\text{Fe}_{13}/\text{BNNS}$  interaction, which will give helpful instructions in the design and synthesis of supported Fe-based catalysts in heterogeneous catalysis. This publication is organized as follows. The calculation details are described in Section 2. The results and discussion are presented in Section 3. Finally, the conclusions are given in Section 4.

## 2. Calculation details

All DFT calculations were carried out using the Vienna *ab initio* simulation package (VASP) with the gradient-corrected PW91 exchange-correction functional. The ionic cores were described with the projector augmented-wave (PAW) method and for valence electrons a plane-wave basis set with a cutoff of 400 eV was employed. Spin-polarization calculation was considered. A  $5 \times 5$  h-BNNS monolayer was used as a substrate in the calculations and the point defect sites can be constructed by removing a single boron or nitrogen atom from h-BNNS. A  $2 \times 2 \times 1$  Monkhorst–Pack  $k$ -point grid was used to sample the Brillouin zone of h-BNNS substrate, which was tested to be converged. In order to avoid the interaction between periodic images, a vacuum space of 14 Å was adopted in the  $z$ -direction. For the calculation of the density of states (DOS),  $11 \times 11 \times 1$  and  $7 \times 7 \times 1$  Monkhorst–Pack  $k$ -points grid for h-BNNS with B-vacancy and N-vacancy, respectively, which were tested to be sufficient to yield accurate results. All atoms were fully relaxed until the maximum force on a single atom was less than 0.05 eV/Å.

The binding energy ( $E_b$ ) for the metal nanoparticle on h-BNNS was calculated by the following equation:

$$E_b = -[E_{\text{nanoparticle/h-BNNS}} - (E_{\text{nanoparticle}} + E_{\text{h-BNNS}})]$$



**Fig. 1.** Optimized configurations for (A) pristine h-BNNS, (B) h-BNNS with B-vacancy, and (C) h-BNNS with N-vacancy. Pink and blue colors represent B and N atoms, respectively.

Where  $E_{\text{nanoparticle/h-BNNS}}$ ,  $E_{\text{nanoparticle}}$  and  $E_{\text{h-BNNS}}$  were energies for the complex, free metal nanoparticle and free h-BNNS substrate, respectively. A larger  $E_b$  means an energetically more favorable process.

The charge difference density ( $\Delta\rho(r)$ ) plots were obtained by subtracting the charge densities of the separated nanoparticles and defective h-BN from the charge density of the Fe systems as following equation:

$$\Delta\rho(r) = \rho_{\text{substrate+particle}}(r) - [\rho_{\text{substrate}}(r) + \rho_{\text{particle}}(r)]$$

Where  $\rho_{\text{substrate+particle}}$ ,  $\rho_{\text{substrate}}$  and  $\rho_{\text{particle}}$  represented the electron charge distributions for the  $\text{Fe}_{13}/\text{BNNS}$  composites, defective h-BNNS and  $\text{Fe}_{13}$  nanoparticle, respectively.

## 3. Results and discussion

### 3.1. Geometry of $\text{Fe}_{13}$ nanoparticle on defect free h-BNNS

Before investigating the  $\text{Fe}_{13}$  nanoparticle anchored on defective h-BNNS, the configurations of  $\text{Fe}_{13}$  on the defect free h-BNNS were extensively explored. The optimized B–N bond length for

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