

# Divacancy-nitrogen-assisted transition metal dispersion and hydrogen adsorption in defective graphene: A first-principles study

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We propose a route to dispersing hydrogen-adsorbing transition metals (TMs) on a large scale onto vacancy-engineered defective graphenes by employing natural carbon-nitrogen-TM complexes, i.e., TM-containing porphyrins. Based on first-principles density-functional calculations, the TM-porphyrin core—made of one central TM and four surrounding nitrogen atoms—can be effectively generated by three defect-engineering processes of graphenes: (1) creation of carbon divacancies, (2) nitrogen substitution of unsaturated carbons, and (3) TM incorporation. The atomistically dispersed Sc, Ti, and V are able to adsorb hydrogen molecules as strongly as 0.2–0.4 eV with the Kubas coordination. The Fe-porphyrin-like unit in graphenes can also have the Kubas adsorption of hydrogen, if the exchange splitting is reduced by a compressive in-plane strain.

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## I. INTRODUCTION

Recently, several groups<sup>1–3</sup> have proposed that transition metals (TMs) dispersed atomistically can store hydrogen nondissociatively—but with appreciable adsorption energy in contrast to traditional van der Waals-type adsorption—so that they would be suitable for practical storage media operating at ambient thermodynamic conditions. In reality, however, the dispersed atomic TMs in the proposed systems are very unstable against cohesive interaction by themselves, and after clustering, they lose their storage capability.<sup>4,5</sup> Therefore, fully utilizing the storage power of TMs is critically dependent on how one can disperse TMs stably against the strong cohesion tendency. It has been also suggested that doping of boron or nitrogen in carbon systems such as fullerenes, nanotubes, and graphenes could improve TM dispersion characteristics.<sup>6,7</sup>

In the quest to design efficient and realizable TM dispersants, we can take a hint from nature. In natural biological systems, atomic TMs conjugated with organic molecules are frequently used for catalysis or carrying gas molecules. Among them, metal-incorporated porphyrins are found in many natural and artificial photosynthetic systems<sup>8</sup> as well as oxygen-carrying proteins such as hemoglobins and myoglobins.<sup>9</sup> An iron-porphyrin, or heme, comprises one central Fe that conjugates with four surrounding, dangling-bond nitrogen atoms, as shown in Fig. 1(a). The nitrogen dangling bonds will be stabilized by taking two *s* electrons from Fe, which thus exists as Fe<sup>2+</sup>, or Fe(II). Because of the strong conjugation with surrounding nitrogen atoms, the atomic Fe(II) is able to serve as a stable agent that carries oxygen in living cells without suffering from clustering. Very recently, Kim *et al.*<sup>10</sup> reported that natural Fe-porphyrin can adsorb hydrogen molecules as strongly as 0.3 eV per H<sub>2</sub> within the generalized gradient approximation, which typically underestimates the hydrogen adsorption energy.<sup>11</sup> The next big question is how does one build in the laboratory the large scale, microporous, porphyrin-derived structures that

can be used for TM dispersion and hydrogen adsorption? Recently, synthesis of porous but tunable porphyrin-based, three-dimensional (3D) metal-organic frameworks was reported<sup>12,13</sup> for potential application to gas storage, molecular recognition, or catalysis.

In this Letter, we propose a synthetic route to incorporating the porphyrin unit as TM dispersants and hydrogen adsorbents into vacancy-engineered defective graphenes and report hydrogen adsorption characteristics of the engineered porphyrin-in-graphene (PIG) systems. Calcium<sup>14,15</sup> and all 3*d* TMs from Sc to Zn were considered in this study.<sup>16</sup> Based on first-principles density-functional calculations, we found that the PIGs are outstanding in atomistically dispersing TMs among previously proposed methods. The dispersed Sc, Ti, and V in PIGs retain the strong hydrogen adsorption strength of 0.19–0.37 eV per H<sub>2</sub>. Also, the Kubas-type hydrogen adsorption in non-magnetic H<sub>2</sub>-Fe-PIG—an analog of the diamagnetic oxyhemoglobin<sup>17</sup>—can be stabilized by applying compressive in-plane strains.

## II. METHOD

We employed the first-principles density-functional theory method with ultrasoft pseudopotentials<sup>18</sup> as implanted in the quantum ESPRESSO package.<sup>19</sup> We used the Perdew-Burke-Ernzerhof (PBE) functional<sup>20</sup> for the exchange-correlation energy. A plane-wave basis set with an energy cutoff of 35 Ry and the (4 × 4 × 1) mesh for **k**-points integration were chosen based on total-energy convergence tests. All atomic

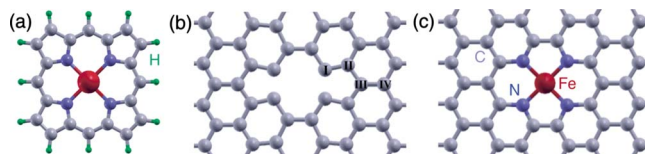


FIG. 1. (Color online) Atomic structures of (a) a model Fe-porphyrin molecule, (b) divacancy in graphene, and (c) Fe-PIG.

TABLE I. Energy difference between the PBE binding energy ( $E_B$  in eV) of atomic TMs to proposed dispersants and the corresponding PBE cohesive energy ( $E_C$ ) to form bulk metals. Because Ref. 6 and 7 used the local-density approximation (LDA) and reported LDA- $E_B$ , we used LDA- $E_C$  (Ref. 36) to calculate  $E_B - E_C$ . Hydrogen adsorption energies ( $E_{\text{ads}}$  in eV) and TM- $\text{H}_2$  separations ( $d_{\text{TM-H}_2}$  in Å) calculated in this work are presented.

	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E_B - E_C$	3.83	3.88	2.95	2.18	2.64	2.78	2.00	2.96	2.95	1.33	1.99
	-0.6 <sup>a</sup>	-2.3 <sup>b</sup>	-2.8 <sup>c</sup>								
		-1.5 <sup>b</sup>	-3.0 <sup>d</sup>								
		2.6 <sup>e</sup>	1.0 <sup>e</sup>	-0.3 <sup>e</sup>							
		2.4 <sup>f</sup>	1.3 <sup>f</sup>	0.5 <sup>f</sup>							
$E_{\text{ads}}$	0.08	0.21	0.37	0.19	0.01	0.02	0.02	0.07	0.04	0.01	0.01
$d_{\text{TM-H}_2}$	2.83	2.35	1.89	1.85	3.75	3.33	3.29	2.44	3.40	3.65	3.41

<sup>a</sup>Reference 14.

<sup>b</sup>Reference 1.

<sup>c</sup>Reference 3.

<sup>d</sup>Reference 2.

<sup>e</sup>Reference 7.

<sup>f</sup>Reference 6.

forces were fully minimized to less than 0.001 Ry/(a.u.). A single PIG was modeled in a  $3 \times 3$  graphene supercell with a 20-Å vacuum space. The in-plane stresses that result from various ionic sizes of TMs in PIGs were fully relaxed. When we used a  $6 \times 6$  graphene supercell to model Ca, Ti, and Fe-PIGs, the TM binding energies are increased 0.4, 0.1, and 0 eV, respectively, compared to the  $3 \times 3$  cases, and the  $\text{H}_2$  adsorption energies are varied in a few meV.

### III. RESULTS AND DISCUSSION

The first step in incorporating the porphyrin unit into graphenes is to generate carbon vacancies. It has been known that high-resolution TEM<sup>21</sup> and proton irradiation<sup>22,23</sup> can create numerous carbon vacancies in graphenes and nanotubes. Recently, Saito *et al.*<sup>24</sup> reported that in graphenes, divacancies ( $V_{2C}$ ) are more likely to be formed than monovacancies ( $V_C$ ); even two  $V_C$  will merge into one  $V_{2C}$ .

To stabilize a  $V_{2C}$  that is energetically unstable, one can next expose the dangling-bonded carbons near the  $V_{2C}$  by nitrogen gas. The calculated formation energy of the nitrogen substitution ( $N_C$ ) with reference to  $\text{N}_2$  gas and graphene<sup>25</sup> is -0.5 eV (Site I). So, the nitrogen substitution reaction will be thermodynamically favored with the exothermic energy. This can be understood as one more valence electron of the substitutional N stabilizes the unpaired electron of the under-coordinated C. For comparison, we also calculated the formation energies of other  $N_C$  sites including the pristine bulk. The calculated values are 0.3, 0.2, 1.1, and 1.0 eV for Site II, III, and IV of Fig. 1(b), and the pristine bulk site, respectively. The  $N_C$  formation with N replacing saturated C atoms in graphenes is thus a probabilistic event with positive formation energies. All four dangling-bonded carbons near the  $V_{2C}$  will be replaced by two  $\text{N}_2$  molecules with an exothermic energy of about 2 eV. The dissociation of  $\text{N}_2$ , however, may need to be assisted by catalysts such as CoMo alloy or iron oxides.<sup>26,27</sup>

The  $4N_C - V_{2C}$  is still very reactive as a strong oxidative agent that requires two additional electrons for full saturation. As typically observed in organic molecules,<sup>8,9</sup> the unit can be stabilized by one divalent TM atom with forming a TM- $4N_C - V_{2C}$  or PIG, as depicted in Fig. 1(c). We calculated binding energies ( $E_B$ ) of TM atoms to the  $4N_C - V_{2C}$  and compared them with the calculated cohesive energies ( $E_C$ ) of TMs, as listed  $E_B - E_C$  in Table I. If  $E_B - E_C$  is negative, the TM will favor clustering or cohesion. If not, the TM-PIG will be stable against TM clustering. As listed in Table I, our PIGs outperform previously proposed methods for dispersing metals from Ca to V. For example, Ca and Sc on top of  $C_{60}$  have negative  $E_B - E_C$  of -0.6 and -2.3 eV,<sup>1,14</sup> respectively, whereas our PIGs have  $E_B - E_C$  of about 3.8 eV for both metals. Because of their high cohesive energies of >5 eV, Ti and V are generally considered as being difficult to disperse; their  $E_B - E_C$  are negative by about -3 eV on polymers<sup>3</sup> and (8,0) nanotubes.<sup>2</sup> In contrast, our Ti- and V-PIGs have  $E_B - E_C$  of 3.0 and 2.2 eV, respectively. Also, there is a report that boron or nitrogen-doped graphenes can be good TM dispersants,<sup>6,7</sup> but their  $E_B - E_C$  are less than in PIGs (see Table I). Fe has the largest cohesive energy of 4.9 eV among later TMs, yet the Fe-PIG can disperse it exothermally by 2 eV. Even if we take into account formation enthalpies of metal hydrides such as  $\text{ScH}_2$  and  $\text{TiH}_2$  of about 1 eV, the binding energies are still stronger by 1-2 eV.

We have examined thermodynamic and kinetic stability of the Fe-PIG under  $\text{H}_2$  environment, as shown in Fig. 2. When hydrogen is present, one hydrogen molecule can passivate two dangling bonds of the  $4N_C - V_{2C}$  with kicking out the core Fe, which can form a bulk metal. The reaction was calculated to be exothermic by 1.1 eV. It means Fe-PIG is not stable thermodynamically under  $\text{H}_2$  condition. Interestingly, Fe-porphyrin is also unstable thermodynamically by 0.9 eV against the hydrogen passivation. Then, how can the Fe-porphyrin be stable in nature? The dissociation reaction is hindered by kinetics. Because of strong covalent bonding

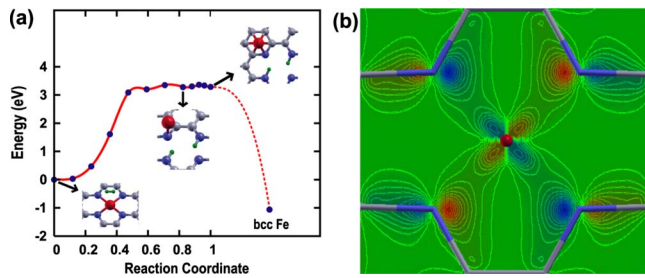


FIG. 2. (Color online) (a) Nudged elastic band (NEB) pathway for the dissociation of Fe from the core of Fe-PIG in an  $H_2$  environment. Two intermediate states are depicted. The reaction path to form bcc-Fe (marked by the dash line) is just for eye-guide based on the calculated formation energy. (b) Charge density plot of a bonding state between N  $\sigma$  and Fe  $d_{xy}$  orbitals with a phase factor. The interval between the contour lines is  $4.9 \times 10^{-3} e/\text{\AA}^3$ .

between Fe  $d_{xy}$  and N dangling  $\sigma$  states as depicted in Fig. 2(b), the dissociation needs to overcome a large kinetic energy barrier at least of 3.3 eV, as shown in Fig. 2(a). The calculated softest vibrational mode of the Fe-PIG is  $114 \text{ cm}^{-1}$ , which is consistent with the measured value from an NO-Fe-porphyrin.<sup>28</sup> Therefore, once Fe-PIG is generated, it will be as stable as the natural Fe porphyrin. Also, the 1:4 ratio of Fe and N has been measured in a recent experiment of N-doped nanotubes.<sup>29</sup>

Even if both the Fe-PIG and Fe-porphyrin have one Fe and four two-coordinated N's, details of their local atomic structures are slightly different. Because of the original graphene network, the four nitrogens in the Fe-PIG form a rectangle with a smaller pore than that of the square porphyrin:  $2.77 \times 2.58$  versus  $2.91 \times 2.91 \text{ \AA}^2$ . The large ions from Ca to V are thus buckled out of the graphene plane, whereas TMs from Cr to Zn sit in plane. Ca, Sc, Ti, and V protrude from the plane by 1.18, 0.79, 0.46, and 0.45  $\text{\AA}$ , respectively. PIG consists literally of four pyridine-like rings in a hexagonal network, whereas porphyrin consists of four pyrrole-like pentagonal rings linked by four methines (-CH-); this contrast is clearly shown in Figs. 1(a) and 1(c).

Next, we investigated hydrogen adsorption on TM-PIGs, and listed the calculated PBE adsorption energies and TM- $H_2$  separations in Table I. It was shown<sup>30</sup> that PBE hydrogen adsorption energies and structural parameters well agree with measured values in TM-exposed metal-organic systems. Very recently, it was also demonstrated that the PBE hydrogen adsorption energies in Ca-decorated nanostructures are as good as those from the Møller-Plesset second order perturbation theory (MP2) calculations with the complete basis set limit.<sup>31–33</sup> Sc-, Ti-, and V-PIGs retain the hydrogen adsorption power of 0.19–0.37 eV per  $H_2$ , corresponding to the Kubas coordination,<sup>34</sup> but later TMs except Co have adsorption energies ranging from 0.01 to 0.04 eV, which is in the range of van der Waals-type interaction. Ca and Co-PIG adsorb hydrogen as 0.08 and 0.07 eV per  $H_2$ , respectively, falling into intermediate between Kubas and van der Waals. From site- and orbital-decomposed electronic structure analyses (see Fig. 3), we proved that the appreciable hydrogen adsorption energies of Sc- to V-PIGs are attributed to the unique electron donation mechanism from

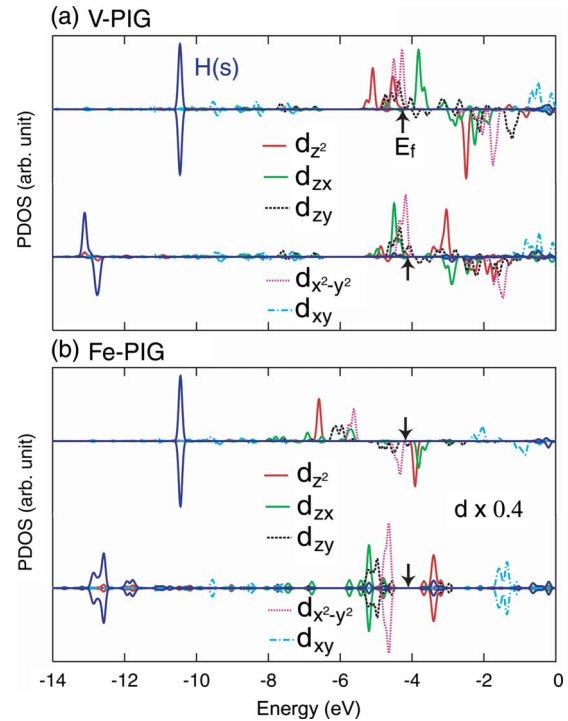


FIG. 3. (Color online) Projected density of states (PDOS) of (a) V-PIG and (b) Fe-PIG before and after dihydrogen adsorption.  $E_f$  represents the Fermi level and also is marked by arrows. The energy zero is the position of the vacuum level. The occupied  $H_2 \sigma$  orbital couples mostly with the TM  $d_{z^2}$  orbital. After hydrogen adsorption, the originally half-occupied  $d_{z^2}$  orbital becomes mostly empty.

the  $H_2 \sigma$  to the depopulated  $d_{z^2}$  orbitals. The donated electrons are 0.05, 0.06, and 0.12 for Sc, Ti, and V, respectively, from the Löwdin population analysis. The bond length of adsorbed  $H_2$  on the V-PIG is stretched to 0.81  $\text{\AA}$ , as shown in Fig. 4(a), from free hydrogen's 0.75  $\text{\AA}$ . The weak adsorption of hydrogen on later TM-PIGs can be understood in terms of symmetry lowering;<sup>10</sup> although the hydrogen coupling can give a net energy gain via electron donation, it can also create a strain in the original crystal field, which increases energy. So, if the adsorption energy gain is not enough as in later TMs because of half-occupied  $d_{z^2}$ , the Kubas coordination will not be preferred over the van der Waals. The buckled Ca-PIG can hold four hydrogen molecules, while the other TM-PIGs can bind two at maximum.<sup>35</sup>

Fe-PIG is special, because magnetic Fe-porphyrin can bind oxygen and hydrogen molecules assisted by demagnetization.<sup>10,17</sup> Normally, the Fe-PIG adsorbs a  $H_2$  in a

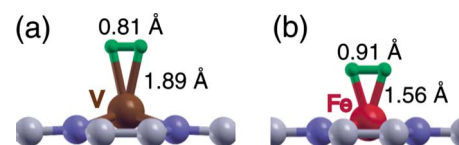


FIG. 4. (Color online) Atomic structures of an adsorbed  $H_2$  on top of (a) V-PIG and (b) Fe-PIG in a Kubas-type side-on configuration. The  $H_2$ -Fe-PIG is metastable against the van der Waals-type adsorption by 0.05 eV.

magnetic state of  $2\mu_B$  via the van der Waals-type coupling. But the Fe-PIG can adsorb a  $H_2$  in a nonmagnetic state via the Kubas-type coupling, as shown in Fig. 4(b). The nonmagnetic Kubas adsorption is less stable by 0.05 eV than the magnetic van der Waals adsorption. For comparison, the energy difference in  $H_2$ -Fe-porphyrin is 0.33 eV.<sup>10</sup> The exchange splitting ( $\Delta_{ex}$ ) of the Fe-PIG is much reduced due to the smaller pore than that of the Fe-porphyrin. The  $\Delta_{ex}$  and thus the Kubas hydrogen adsorption can be modified by ligation<sup>10</sup> or pore-size control by external strains. To see this, we applied external compressive or tensile in-plane strain, and calculated hydrogen adsorption energies of magnetic van der Waals and non-magnetic Kubas configurations, respectively. Figure 5 shows that the Kubas adsorption is stabilized after applying 1.2% compressive strain. When we apply 3% compressive strain, the energy advantage of the Kubas adsorption is already about 0.2 eV.

#### IV. CONCLUSION

We proposed a synthetic route to incorporating the naturally stable porphyrin unit into vacancy-engineered defective graphenes with three engineering processes: (1) creation of carbon divacancies, (2) nitrogen substitution, and (3) TM incorporation. From first-principles calculations, we determined that PIGs outperform previously proposed methods for TM dispersion. Sc-, Ti-, and V-PIGs can adsorb hydrogen molecules via electron-donation coupling with energy gains of 0.2–0.4 eV per  $H_2$ . By manipulating the exchange splitting of Fe-PIG with compressive strains, we could stabilize the Kubas hydrogen adsorption on the Fe-PIG.

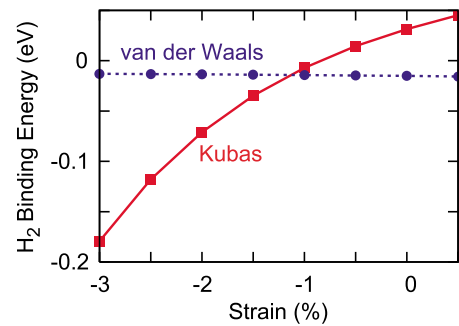


FIG. 5. (Color online) Hydrogen adsorption energies of non-magnetic Kubas-type (red square) and magnetic van der Waals-type (blue circle) couplings as a function of externally applied in-plane strain. Upon inducing compressive (denoted as negative sign) strains (of 1% or larger), the nonmagnetic adsorption (Kubas-type interactions) starts to be preferred against the magnetic hydrogen adsorption.

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