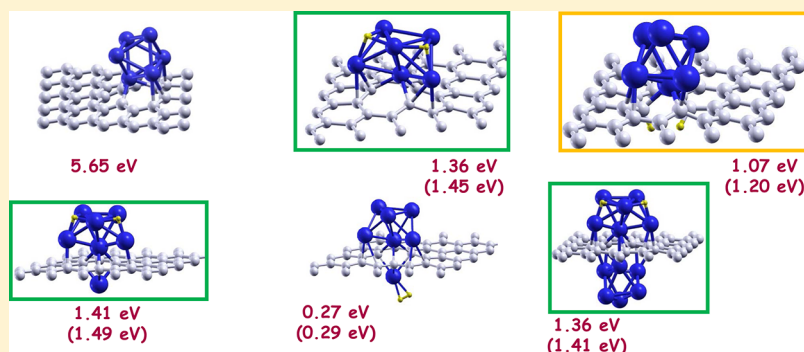


# Competition between Palladium Clusters and Hydrogen to Saturate Graphene Vacancies

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**ABSTRACT:** Doping with palladium has been proposed as a means to enhance the hydrogen storage capacity of nanoporous carbon materials. Palladium atoms and clusters attach strongly to defects on the walls of nanoporous carbons, which can be mimicked as graphene layers with vacancies. On the other hand, atomic hydrogen also binds strongly to the dangling bonds of defects and edges of graphitic carbon. Therefore, hydrogen adsorbed on Pd-doped nanoporous carbons could compete with the Pd dopant to saturate the vacancies. In this work we have performed density functional calculations to investigate the competition between palladium atoms and clusters, on one hand, and hydrogen, on the other hand, to saturate graphene vacancies. We find that palladium binds stronger than hydrogen to graphene vacancies and, therefore, hydrogen can not replace the palladium atoms or clusters attached to the vacancies. Instead, hydrogen adsorbs on the palladium. Thus, hydrogen adsorption on Pd-doped carbons does not destroy the stability of the material. Moreover, our study shows that graphene vacancies decorated with Pd just on one side of the graphene layer are not fully saturated. The other side of the vacancy remains quite reactive and therefore Pd atoms and clusters can be attached, simultaneously, to both sides of the vacancy. Interestingly, the hydrogen adsorption mechanisms and energies do not depend on whether Pd atoms and clusters are decorating one side or both sides of the vacancies.

## 1. INTRODUCTION

Nowadays, the threats from global warming due to the consumption of fossil fuels have increased. This problem requires adopting new strategies to find other sources of energy that could replace fossil fuels, and hydrogen is considered a good candidate.<sup>1,2</sup> Hydrogen is an energy carrier that holds tremendous promise as a new renewable and clean energy option. The basic mechanism of this fuel is the reaction of hydrogen with atmospheric oxygen in a hydrogen fuel cell, producing an electric current, and the only emission is water. However, hydrogen is a gas, and the problem with this technology is to find an efficient way to store hydrogen in a tank at room temperature and moderate pressures, to be able to run the car for about 600–700 km.<sup>3</sup> For those reasons, the USA Department of Energy established three main targets for an efficient hydrogen storage as (a) a gravimetric density of at least 7.5%, (b) a volumetric density of 0.07 kg of hydrogen per liter, and (c) a reversible operation at ambient temperature and moderate pressures.<sup>4</sup> A promising method to store hydrogen is to adsorb it in light porous solid materials like porous carbon

structures, because these have a lightweight and a large surface area. Those materials have a reasonable storage capacity of hydrogen at low temperatures (about 77 K), but their capacity diminishes drastically at room temperature and normal pressure.<sup>5,6</sup> Thermodynamic estimations indicate that the adsorption energies that would lead to an efficient cyclic adsorption/desorption operation at room temperature and moderate pressures are in the range of 0.2–0.6 eV per hydrogen molecule, which is a narrow energy window intermediate between typical physisorption (less than 0.2 eV) and chemisorption (more than 0.6 eV).<sup>7,8</sup>

Experimental work by Contescu et al.<sup>9,10</sup> indicated that doping the carbon materials with metallic species is a promising

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strategy to enhance the hydrogen adsorption because these metal species have the effect of increasing the binding energies of molecular hydrogen to the pore walls.<sup>11–17</sup> In addition, the deposited metallic atoms and small clusters also can bind several hydrogen molecules, and this increases the hydrogen storage capacity of the material.<sup>10,18</sup> The binding of molecular hydrogen to transition metals has been explained using the Kubas model as a donation of electronic charge to the unfilled d orbitals of transition metals such as Pd, followed by back-donation from the transition metal to the antibonding orbital of H<sub>2</sub>.<sup>19</sup> However, there are some difficulties with the metal doping of graphitic materials. The first one is that aggregation of the adsorbed dopant atoms and small clusters may occur, because metal–metal bonding is usually stronger than the metal–carbon bonding.<sup>20–22</sup> Theoretical studies based on density functional theory reported that transition metal adatoms on pristine graphene have binding energies ranging from 0.2 to 1.5 eV, and their calculated migration barriers proved to be low, in the range of 0.2–0.8 eV, indicating that those adatoms should be mobile even at room temperature when deposited on pristine graphene. These results reveal a tendency of adsorbed transition metal atoms to form large clusters on the graphene surface, leading to a reduction in the potential hydrogen storage capacity of the doped material. The second problem is that desorption of metal–hydrogen complexes often competes with desorption of H<sub>2</sub>. Both problems will be reduced by increasing the binding energy of the metal atoms or small metal clusters to the supporting carbon substrate, and this is achieved by anchoring the metal atoms and small clusters to the abundant existing defects in the carbon networks of the graphitic pore walls. In fact, it has been found that defects in graphene, such as mono- and divacancies, increase the adsorption energies of metal atoms and small metal clusters significantly, to the point of exceeding the cohesive energy of the metal.<sup>23–26</sup>

Hydrogen adsorption energies are dependent on both the size of the Pd cluster and the adsorption site on the cluster.<sup>18,27,28</sup> A comparison between adsorption on free Pd clusters,<sup>29,30</sup> adsorption on Pd clusters supported on pristine graphene,<sup>27</sup> and adsorption on Pd clusters anchored on vacancies<sup>18,26,30</sup> reveals that the vacancies play a role in modulating hydrogen adsorption through their interaction with the Pd clusters. One of the effects is steric, that is, the Pd atoms bonded to the vacancy are less exposed to hydrogen. The second, and equally important effect is chemical, that is, the Pd atoms bonded to the vacancy lose part of their affinity toward hydrogen. For instance, we have reported<sup>26</sup> that the adsorption binding energy of molecular hydrogen on a single Pd atom anchored on a graphene vacancy is 0.21 eV. This value contrasts with the adsorption energies of 0.96 eV on Pd-doped pristine graphene and 1.12 eV on a free Pd atom. That is, the Pd atom utilizes a part of its bonding capacity by interacting with the dangling bonds of the graphene vacancy, and consequently its bonding with the H<sub>2</sub> molecule is weaker compared to the bonding of H<sub>2</sub> with Pd adsorbed on pristine graphene or with free Pd.

Other workers have also investigated the interaction of hydrogen with metal atoms and clusters (lithium,<sup>31</sup> aluminum,<sup>32</sup> nickel<sup>33</sup>) anchored on graphene vacancies, and their consequences for hydrogen storage. Very recently, Rangel and co-workers<sup>34</sup> investigated the effect of having more complex vacancy defects, namely, vacancies in which some of the surrounding carbon atoms have been replaced by nitrogen.

Their calculations show that the presence of the nitrogen atoms lowers the formation energies of those vacancies.

Although palladium clusters attach strongly to graphene vacancies,<sup>26</sup> atomic hydrogen produced by the dissociation of H<sub>2</sub> on the Pd clusters<sup>18,27</sup> could also interact strongly with the dangling bonds of those vacancies, affecting perhaps the stability of the material. In order to unravel the competition between hydrogen and the metal to decorate vacancies in the inner walls of porous carbons we have performed density functional calculations for different configurations relevant to that competition. The result is that Pd atoms and clusters attach to graphene vacancies with higher binding energies than hydrogen and, therefore, hydrogen adsorption and dissociation on Pd-doped carbons does not affect the stability of the doped material. In addition, our study shows that the bonding capacity of graphene vacancies does not saturate through Pd attachment on only one side of the layer, and that additional Pd atoms or clusters can also be attached on the other side of the layer. Both are favorable conclusions for the technology of hydrogen storage in doped porous carbons. In Section 2 we present the key features of the Density Functional Formalism used in the calculations, Section 3 presents the results and the conclusions are reported in Section 4.

## 2. THEORETICAL MODEL

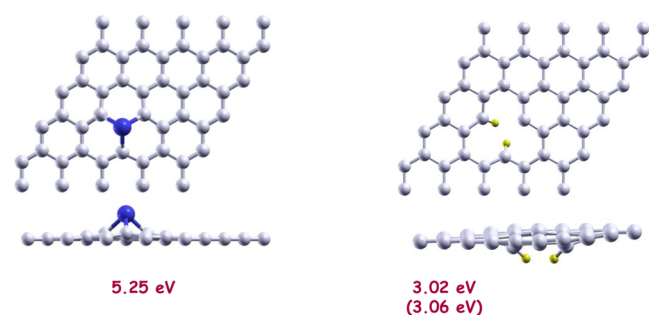
We have investigated the mechanisms of saturation of graphene single-vacancies by hydrogen, a palladium atom and Pd<sub>6</sub> clusters using the density functional theory (DFT). Attaching those species on one side and on both sides of the vacancy is investigated. The graphene layer is a good model often used to simulate the graphitic walls of nanoporous carbon materials, and vacancies are representative defects of those walls. Palladium deposited on graphene tends to aggregate and form three-dimensional clusters,<sup>20</sup> especially near vacancies, where they become strongly attached.<sup>26</sup> The DFT calculations have been performed with the DACAPO<sup>35</sup> code, using the supercell method and a plane wave basis set. The graphene layer is represented by a supercell containing 5 × 5 hexagonal unit cells, each of which contains two C atoms. The total supercell has 50 carbon atoms (included the one that is removed to create the vacancy). The supercell size in the *x* direction is 12.33 Å, and in the *z* direction the supercell is taken to be large enough (14 Å) to avoid interactions between the images of the graphene layer in different supercells. The interactions of the valence electrons with the ionic cores are described with Vanderbilt ultrasoft pseudopotentials.<sup>36</sup> An energy cutoff of 350 eV was taken for the plane wave expansion of the wave functions, and a cutoff of 1000 eV for the electron density, for good convergence. The Monkhorst-Pack<sup>37</sup> k-point set was [2,2,1], and because the supercells used in the calculations are quite large, this selection is sufficient to guarantee convergence in the binding energies better than 10 meV. Electronic exchange and correlation effects are treated by the generalized gradient approximation of Perdew and Wang (GGA-PW91).<sup>38</sup> The DFT-PW91 calculations do not incorporate dispersion interactions but based in other studies one would expect a small contribution (less than 0.2 eV) to the adsorption energies. However, to assess that, indeed, the effect of the dispersion interactions is small, we have also performed dispersion corrected density functional theory calculations using Grimme's DFT-D3<sup>39</sup> combined with the PBE<sup>40</sup> functional for exchange-correlation. The reason for using PBE is that the DFT-D3 method has not been implemented for the

PW91 functional. We have used the modified version<sup>41</sup> of the so-called BJ-damping.<sup>42</sup> Both DFT-PW91 and DFT-PBE corrected for dispersion (DFT-D3) energies are given in the manuscript. Our calculations confirm that the contribution of the dispersion interactions to the adsorption energies of hydrogen is lower than 0.2 eV. An extensive search of the possible combinations and interactions between hydrogen, Pd and both sides of the vacancy has been performed. The search also included the adsorption of a second hydrogen molecule. Then, the structures of all the systems explored were fully optimized until the forces acting on the atoms were smaller than 0.05 eV/Å.

### 3. RESULTS AND DISCUSSION

Hydrogen adsorbs readily on palladium atoms and clusters supported on graphene vacancies.<sup>18</sup> However, atomic hydrogen, produced by the dissociation of H<sub>2</sub> either on the Pd clusters or on the vacancy, can also saturate the dangling bonds of the C atoms around the vacancy. Moreover, adsorption of palladium and/or hydrogen may take place at a graphene vacancy on both sides of the graphene layer. Therefore, we have first investigated the saturation of the vacancies with palladium and hydrogen on both sides of the graphene layer, and then the competition between palladium and hydrogen for the vacant site. Atomic palladium and Pd<sub>6</sub> clusters are considered as case studies.

**Palladium on Graphene Vacancies.** Palladium atoms attach strongly to graphene vacancies with an adsorption energy of 5.25 eV<sup>26</sup> (see Figure 1). The Pd atom sits above the



**Figure 1.** Top and side views of the optimized structures of one Pd atom and one dissociated hydrogen molecule adsorbed on a graphene vacancy, respectively. The corresponding adsorption energies are given in the figure. The PBE+DFT-D3 dispersion corrected adsorption energy of hydrogen is given in parentheses.

center of the vacancy, interacting with the dangling bonds of the three C atoms around the vacant site. The graphene layer deforms a little near the vacancy; the C atoms in direct contact with the Pd atom move out of plane toward Pd by 0.3–0.4 Å, and the next neighboring C atoms (counted from the vacancy) move by 0.1–0.2 Å. The adsorption binding energy given above was calculated as

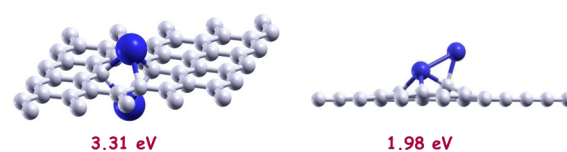
$$E_{\text{ad}}(\text{Pd}) = E(\text{G}) + E(\text{Pd}) - E(\text{Pd on G}) \quad (1)$$

where  $E(\text{G})$  is the total energy of graphene with a vacancy,  $E(\text{Pd})$  is the energy of the Pd atom, and  $E(\text{Pd on G})$  is the energy of the system formed by Pd adsorbed on the graphene vacancy. Other adsorption binding energies will appear below, and for all of them the definition is analogous, that is, the adsorption energy is obtained by first adding the energies of the two separated systems, substrate and adsorbate, and then

subtracting the energy of the composite system after adsorption.

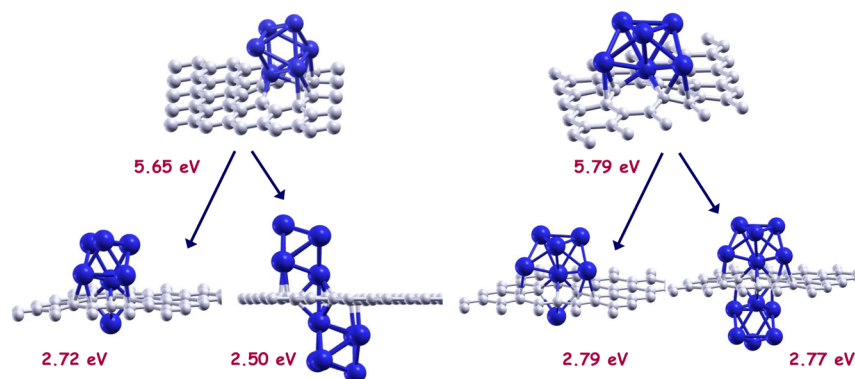
Pd atoms exhibit a strong tendency to form three-dimensional clusters around the graphene vacancies and the clusters attach to the vacancies with substantial adsorption energies<sup>26</sup> of 5.2–5.9 eV. For instance, the lowest energy, octahedral (OCT) structure of Pd<sub>6</sub>, binds to the vacancy with an adsorption energy of 5.65 eV (see Figure 3). The cluster structure experiences only a minor distortion upon deposition on the graphene layer. Pd<sub>6</sub> rests on one of its triangular faces. One of the Pd atoms of that face sits above the center of the vacancy and the other two Pd atoms are above two C–C bonds around the vacancy. The C atoms in direct contact with the cluster move out of plane (in the direction of the Pd atoms) by 0.5–0.7 Å and the next shell of C atoms (counted from the vacancy) move by 0.3–0.4 Å. The magnetic moment of 2 μ<sub>B</sub> of the free Pd<sub>6</sub> cluster is quenched down to zero upon adsorption on the vacancy due to the strong interaction between the cluster and the vacancy. Similarly, the first isomeric structure of Pd<sub>6</sub> (an incomplete pentagonal bipyramid, IPB) binds to the vacancy with an adsorption energy of 5.79 eV, evaluated with respect to free Pd<sub>6</sub> in the same IPB configuration (see Figure 3). The IPB structure rests on a lateral face of one of the pyramids with the apex atom sitting above the center of the vacancy.

However, graphene vacancies do not become fully saturated by attaching palladium atoms or clusters on one side on the graphene layer only. Pd atoms and clusters can be attached to the vacancy from both sides of the graphene layer (see Figures 2 and 3). Thus, a vacancy already doped with one Pd atom



**Figure 2.** Optimized structures of graphene vacancies doped with one Pd atom on each side of the graphene layer and with a Pd<sub>2</sub> dimer on one side. The adsorption energies of the second Pd atom with respect to the vacancy doped with one Pd atom are also included in the figure.

admits a second Pd atom from the other side of the graphene layer with an adsorption energy of 3.31 eV. This energy is higher than the adsorption energy of 1.98 eV for the second Pd atom on the same side of the graphene layer. In this case, the two Pd atoms form a Pd<sub>2</sub> dimer bound to the graphene layer. Thus, saturating the vacancy with two Pd atoms, one on each side of the graphene layer, leads to a configuration more stable than that obtained by attaching the two atoms on the same side. Moreover, the adsorption energies of one Pd atom on the other side of a vacancy having an OCT, or an IPB Pd<sub>6</sub> cluster already attached are 2.72 and 2.79 eV, respectively. Those adsorption energies are a little lower compared to the adsorption of Pd on the other side of a vacancy with a single Pd atom attached, 3.31 eV). This indicates that the other side of vacancies having Pd clusters on one side are less reactive than those having single Pd atoms. This fact becomes also evident when adsorbing a second Pd<sub>6</sub> (OCT) cluster on the other side of a vacancy with one Pd<sub>6</sub> (either in the OCT or in the IPB structure) already attached. The adsorption energy of the second cluster drops to 2.5 and 2.77 eV, respectively, about half of the adsorption energy of the



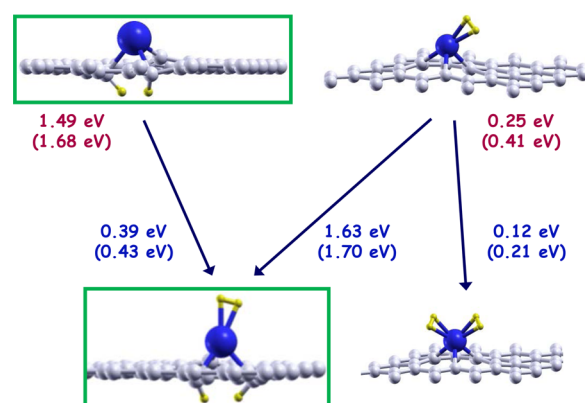
**Figure 3.** Optimized structures of graphene vacancies doped with a Pd<sub>6</sub> cluster on one side of the graphe layer, and clean or doped with a Pd atom or a Pd<sub>6</sub> cluster on the other side. The following adsorption energies are also included in the figure: for the vacancies doped on one side only, the adsorption energy with respect to the free cluster in the same configuration; for the vacancies doped on both sides, the adsorption energy of the atom, or cluster, on the second side. In the latter case, the reactions are indicated by the arrows.

first one. In spite of the drop, it is worth noticing that the bonding capacity of the vacancy still remains strong.

**Competition between Hydrogen and Palladium to Saturate Graphene Vacancies.** Graphene vacancies can be also saturated with hydrogen. Similarly to hydrogen adsorption on the edges of graphene nanoribbons,<sup>43</sup> hydrogen molecules adsorb dissociatively on a vacancy, that is, the H–H bond breaks up, and each individual hydrogen atom binds to one of the C atoms that form the vacancy (see Figure 1). Those two C atoms move out of plane by 0.3–0.4 Å in the direction of the H atoms. The activation barriers in the dissociation process are expected to be small. In a previous study<sup>43</sup> we found that the barriers for the dissociation of H<sub>2</sub> on the clean edges of graphene nanoribbons are smaller than 0.2 eV, and Jiang et al.<sup>44</sup> have obtained barriers of 0.8 eV for the dissociation of H<sub>2</sub> on graphene vacancies; in all these cases, the dissociation reaction can proceed at room temperature. The adsorption energy of the dissociated molecule is 3.02 eV; although lower than the adsorption energies of Pd atoms and clusters on the vacancy, it is quite substantial. Therefore, hydrogen might compete with the Pd atoms or clusters to decorate the vacancy.

First we consider the adsorption of hydrogen on vacancies with one Pd atom attached on one side (the upper side in Figure 4). The relevant configurations are shown in Figure 4. Molecular hydrogen adsorbs on top of the Pd atom with an adsorption energy of 0.25 eV. The Pd atom is not able to dissociate the hydrogen molecule. However, the molecule dissociates directly on the vacancy from the other side (bottom side) of the graphene layer with an adsorption energy of 1.49 eV. Each H atom interacts with the dangling bond of one C atom of the vacancy, and this arrangement, with the Pd atom and the (dissociated) hydrogen molecule on opposite sides of the vacancy, is the most stable configuration.

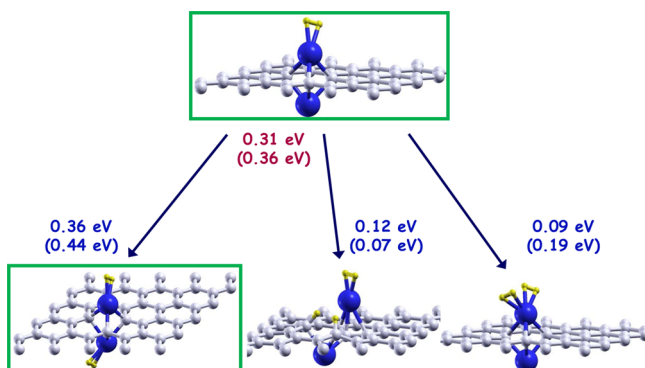
A second hydrogen molecule can be added into this configuration, attached to the Pd atom with an adsorption energy of 0.39 eV. This is the most stable configuration, which can be also viewed as the dissociative adsorption of a hydrogen molecule directly on the lower side of vacancy having a PdH<sub>2</sub> complex on the upper side. The corresponding adsorption energy is 1.63 eV. Evidently, the two sums of successive adsorption energies, 1.49 eV + 0.39 eV, and 0.25 eV + 1.63 eV, give the same result. By contrast, if the second hydrogen molecule is added on the same side of the layer occupied by the Pd dopant, that molecule becomes attached to the PdH<sub>2</sub>



**Figure 4.** Optimized structures of hydrogen adsorbed on a graphene vacancy doped with one Pd atom. The adsorption energies for the first and second hydrogen molecules are shown in the picture. The starting point of the arrows indicate the reference system for adsorption of the second hydrogen molecule. Values in parentheses give the PBE+DFT-D3 dispersion corrected adsorption energies.

complex with a small adsorption energy of 0.12 eV. Configurations with a dissociated hydrogen molecule adsorbed directly on the vacancy from the same side of the Pd atom are highly unstable. Our results show that graphene vacancies are not fully saturated by adsorption of Pd on one side of the layer. Hydrogen can adsorb dissociatively on the other side of the vacancy. On the other hand, if molecular hydrogen is supplied from the same side of the layer as the Pd dopant, it does not displace the Pd atom from the vacant site, but instead the molecules get adsorbed on top of the Pd atom forming Pd(H<sub>2</sub>) and Pd(H<sub>2</sub>)<sub>2</sub> complexes.

The structural configurations and adsorption energies for hydrogen adsorption on a graphene vacancy doped with two Pd atoms, one on each side of the layer, are shown on Figure 5. A first hydrogen molecule adsorbs on the doubly decorated vacancies on top of one of the Pd atoms (the Pd atom on the upper side of the layer) with an adsorption energy of 0.31 eV. This value is slightly larger than the molecular adsorption energy (0.25 eV) when the vacancy is decorated by only one Pd atom. The small increase can be explained by the reduced Pd-vacancy bonding strength occurring when two Pd atoms (instead of one Pd) decorate the vacancy; that reduced bonding strength allows for a stronger bonding between Pd and the hydrogen molecule. A second hydrogen molecule is adsorbed on the second Pd

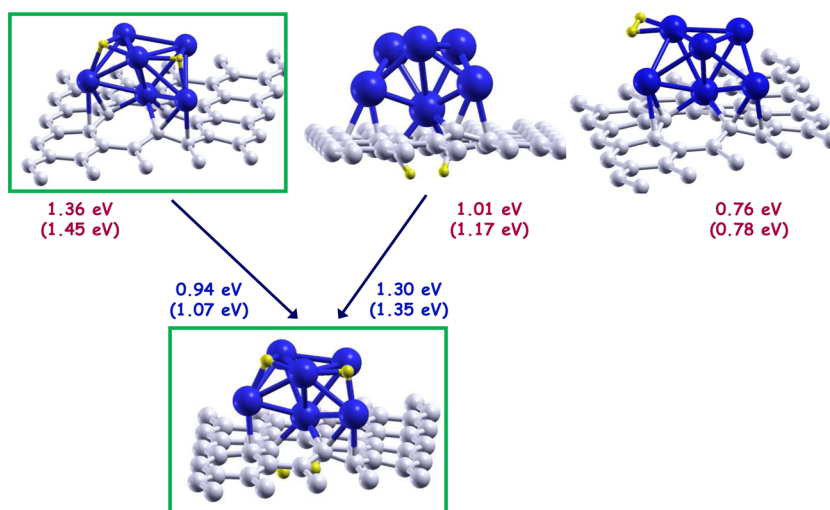


**Figure 5.** Optimized structures of hydrogen adsorbed on a graphene vacancy doped with two Pd atoms, one on each side of the layer. The adsorption energies for the first and second hydrogen molecules are shown in the picture. The starting point of the arrows indicate the reference system for adsorption of the second hydrogen molecule. The PBE+DFT-D3 dispersion-corrected adsorption energies are given in parentheses.

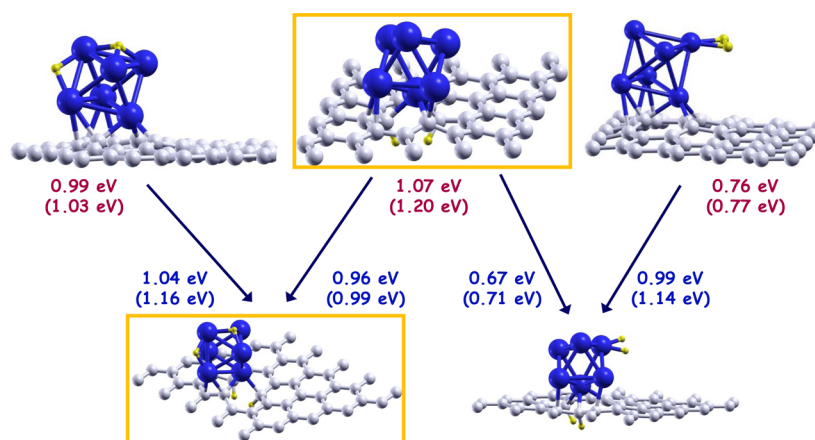
atom (the one on the lower side of the vacancy) with an adsorption energy of 0.36 eV (this configuration is the ground state of the system), while the adsorption energy of that molecule on the first Pd atom is only 0.09 eV. The first adsorbed hydrogen molecule can not dissociate directly on the vacancy decorated on both sides with Pd atoms. However, a second hydrogen molecule adsorbed from the same side as the first one can dissociate and attach directly to the vacancy with a small adsorption energy of 0.12 eV, displacing the PdH<sub>2</sub> complex from the center of the vacant site. This dissociation on the same side of the Pd atom was not possible for a single hydrogen molecule. The reason has again to do with the bonding capacity of the Pd atom. When an H<sub>2</sub> molecule is adsorbed on the Pd atom, the bonding capacity of this Pd atom for a second H<sub>2</sub> molecule becomes a bit reduced, and the dissociative channel of H<sub>2</sub> directly on the vacancy becomes competitive. However, it is worth stressing that the most stable configuration corresponds to the molecular adsorption of the

two molecules, one on each Pd atom, respectively. Thus, our results show that the adsorption energy of a hydrogen molecule on a Pd atom attached to a vacancy fits within a narrow interval of energies of 0.25–0.39 eV, then it is independent of whether the other side of the vacancy is clean or it is decorated with a dissociated hydrogen molecule, with a Pd atom or with a PdH<sub>2</sub> complex. On the other hand, the adsorption energy of a second hydrogen molecule on a Pd atom doping the vacancy is similar (0.12 and 0.09 eV, respectively) for clean vacancies and vacancies decorated with one Pd atom on the other side.

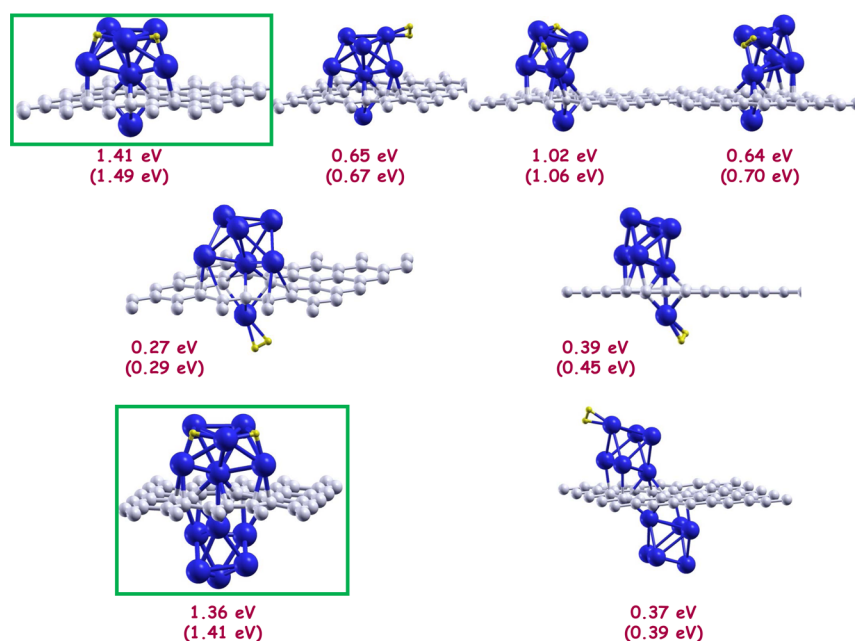
It was found in previous work<sup>18,27</sup> that hydrogen can be adsorbed on supported Pd clusters following two channels: the molecular and the dissociative channels. For low hydrogen loading, the dissociative channel leads to more stable states than the molecular channel. Moreover, the dissociative adsorption of hydrogen on Pd<sub>6</sub> anchored on a graphene vacancy induces a structural change in the cluster from the OCT to the IPB structure. The calculated activation barrier<sup>27</sup> for the dissociation of H<sub>2</sub> on Pd<sub>6</sub> supported on pristine graphene is 0.3 eV, and estimations for the dissociation on Pd<sub>6</sub> anchored to a vacancy give a similar value. Figure 6 shows the most relevant configurations for hydrogen adsorption on a system formed by a graphene vacancy decorated on one side with a Pd<sub>6</sub> cluster in the IPB structure. For comparison, the results for adsorption when the Pd<sub>6</sub> cluster is in the OCT structure are given in Figure 7. If we start with adsorbed OCT Pd<sub>6</sub>, which is the lowest energy structure in the absence of hydrogen, the dissociative adsorption of a hydrogen molecule on the other (lower) side of the vacancy does not change the structure of the Pd cluster (see Figure 7). Moreover, for both OCT Pd<sub>6</sub> and IPB Pd<sub>6</sub> the adsorption energies of a hydrogen molecule dissociated on the other side of the vacancy, 1.07 and 1.01 eV respectively, are quite similar. Even more, this similarity of the adsorption energies holds not only for the case of clean OCT Pd<sub>6</sub> and IPB Pd<sub>6</sub> supported clusters. In fact, starting with clusters already decorated with a dissociated hydrogen molecule, the dissociative adsorption energies of a second molecule on the opposite (lower) side of the vacancy are 1.04



**Figure 6.** Optimized structures of hydrogen adsorbed on a graphene vacancy doped with IPB Pd<sub>6</sub> on one side of the layer. The adsorption energy of the first adsorbed hydrogen molecule is given with respect to the clean system having the Pd cluster in the IPB configuration. The starting point of the arrows indicate the reference system used to calculate the adsorption energy of the second hydrogen molecule. The green color frames enclose the lowest energy configurations of the system with one and two adsorbed hydrogen molecules, respectively. The PBE+DFT-D3 dispersion corrected adsorption energies are given in parentheses.



**Figure 7.** Optimized structures of hydrogen adsorbed on a graphene vacancy doped with OCT Pd<sub>6</sub> on one side of the layer. The adsorption energy of the first adsorbed hydrogen molecule is given with respect to the clean system having the Pd cluster in the OCT configuration. The starting point of the arrows indicate the reference system used to calculate the adsorption energy of the second hydrogen molecule. The orange color frames enclose the corresponding lowest energy configurations restricted to the OCT structure of the Pd<sub>6</sub> cluster. The PBE+DFT-D3 dispersion-corrected adsorption energies are given in parentheses.



**Figure 8.** Optimized structures of hydrogen adsorbed on a graphene vacancy doped with Pd<sub>6</sub> (OCT and IPB structures are shown) on one side of the layer and with either a Pd atom or another Pd<sub>6</sub> cluster on the other side. The adsorption energies are given with respect to the clean system (before hydrogen adsorption) with the adsorbed Pd<sub>6</sub> cluster(s) in the same configuration. The frames in green color mark the lowest energy configurations of one adsorbed hydrogen molecule on Pd<sub>6</sub> when the opposite side of the layer is decorated with one Pd atom or Pd<sub>6</sub>, respectively. The PBE+DFT-D3 dispersion corrected adsorption energies are given in parentheses.

and 0.94 eV, respectively. Those energies are, however, lower compared to the case of the vacancy doped with a single Pd atom (1.49 and 1.63 eV for clean Pd and Pd decorated with an adsorbed H<sub>2</sub> molecule, respectively). This indicates that the lower side of the graphene vacancy is less reactive when the upper side is decorated with Pd clusters as compared to the decoration with single Pd atoms.

Another interesting observation is that the adsorption of hydrogen on the Pd cluster is not affected by the presence of hydrogen on the opposite (lower) side of the vacancy. For instance, the dissociative hydrogen chemisorption energies on the IPB cluster are 1.30 and 1.36 eV whether or not the lower side of the vacancy holds hydrogen. Those two energies are quite similar. The corresponding chemisorption energies on

OCT Pd<sub>6</sub> are 0.96 and 0.99 eV, respectively, quite similar again. Finally, the binding energies for molecular adsorption on OCT Pd<sub>6</sub> are 0.67 and 0.76 eV whether or not the lower side of the vacancy holds hydrogen. In conclusion, the same hydrogen adsorption mechanisms on Pd<sub>6</sub> anchored on a vacancy and similar adsorption energies are found independently of whether the opposite side of the vacancy holds hydrogen.

A behavior similar to the one just described above is observed for adsorption of hydrogen on Pd<sub>6</sub> anchored on a vacancy that holds on the opposite side either a single Pd atom or another Pd<sub>6</sub> cluster (see Figure 8), and we illustrate this feature with some examples. First, we find adsorption energies of 1.41 and 1.36 eV for the dissociative chemisorption on IPB Pd<sub>6</sub> when the opposite side of the vacancy is decorated with Pd

or OCT Pd<sub>6</sub>, respectively. Considering next the molecular adsorption on OCT Pd<sub>6</sub>, the binding energies in those two cases are 0.64 eV (Pd on the opposite side), and 0.37 eV (OCT Pd<sub>6</sub> on the opposite side). It should be noticed that, in each of the two examples presented, the hydrogen adsorption energies are quite similar to those obtained for adsorption on Pd<sub>6</sub> when the opposite side of the vacancy is either clean or doped with hydrogen. On the other hand, the energy for the molecular adsorption of H<sub>2</sub> on one Pd atom anchored on a vacancy is similar for all the cases studied: when the other side of the vacancy is decorated with OCT Pd<sub>6</sub>, with IPB Pd<sub>6</sub>, with a dissociated hydrogen molecule, with a single Pd atom or even clean (non decorated). For those various situations, the molecular adsorption energies are between 0.39 and 0.25 eV, a rather small variation.

The competition between palladium and hydrogen to saturate the vacancies is settled in favor of palladium. If palladium and hydrogen are present on the same side of the graphene layer, then the most stable configurations are those with palladium attached to the vacancy and hydrogen adsorbed on the Pd dopant. Configurations in which a dissociated hydrogen molecule displaces the Pd or Pd<sub>6</sub> dopants to adsorb directly on the vacancy from the same side of palladium are highly unstable. The only exception we have found is for the vacancy doped with one Pd atom on each side. In this case, a second hydrogen molecule displaces the preformed PdH<sub>2</sub> complex from the vacancy and attaches directly on the vacancy as a dissociated molecule with a moderate energy of 0.12 eV. On the other hand, if hydrogen is supplied from the other side of a Pd-doped vacancy, it chemisorbs dissociatively on the vacancy with substantial adsorption energies of 1.5–1.6 eV for the vacancy doped with a Pd atom, and 1.0 eV for the vacancy doped with a Pd<sub>6</sub> cluster (see Figures 4, 6, and 7). However, doping the two sides of the graphene vacancies with palladium are the preferred configurations (see Figures 5 and 8). It is interesting to note that very close adsorption energies are obtained based on DFT-PW91 calculations and based on DFT-PBE with the dispersion corrections given by DFT-D3. The dispersion corrected energies are about 0.1 eV higher than the pure DFT energies. This small difference does not affect the discussions and the conclusions throughout the manuscript.

#### 4. CONCLUSIONS

Palladium-doped nanoporous carbon materials are good candidates for hydrogen storage. The Pd atoms and clusters attach preferentially to the defects, e.g., vacancies, of the graphitic walls of the nanopores. It has been found that palladium doping enhances the adsorption of hydrogen on the nanoporous carbons. However, the adsorbed hydrogen might compete with palladium to decorate the vacancies, compromising the stability of the material. We have performed density functional calculations to investigate the competition between palladium and hydrogen to saturate graphene vacancies. Graphene with vacancies is used here as an appropriate model for the walls of nanoporous carbons and their defects. To assess the contribution of the dispersion interactions, we have compared the results obtained with DFT-PW91 and with DFT-PBE corrected for dispersion using DFT-D3. We found that dispersion interactions are small and therefore do not modify the conclusions of the present study.

Graphene vacancies are very reactive, and Pd atoms, Pd clusters, and hydrogen bind strongly to those defects. Moreover, the vacancies are not fully saturated by attachment

of Pd atoms, Pd clusters, or hydrogen only on one side of the graphene layer, and those species can decorate both sides of the vacancy simultaneously. It is fair to notice that vacancies already predoped with palladium on one side are less reactive than clean vacancies; however, the adsorption energies of Pd atoms, Pd clusters, and hydrogen on the other side of those vacancies are still quite substantial. When hydrogen is present on the other side of a vacancy predoped on one side with a Pd atom or a Pd cluster, it becomes adsorbed on the vacancy as a dissociated molecule, similarly to its adsorption on undoped vacancies. However, because palladium attaches stronger than hydrogen to graphene vacancies, when palladium and hydrogen are both present on the same side of a vacancy, the Pd atom (or the Pd cluster) is the species binding directly to the vacancy, and hydrogen adsorbs on palladium. This behavior has been found on vacancies doped with Pd on one side only and on vacancies doped with palladium on both sides. Comparing the adsorption of hydrogen on Pd-doped graphene vacancies for vacancies decorated on one side and vacancies decorated on two sides, we have found: (a) the same adsorption mechanism (molecular adsorption) and similar binding energies for adsorption of hydrogen on Pd atoms decorating the vacancies, independently of whether the vacancy was decorated on one side or two sides, and (b) the same two adsorption mechanisms (molecular and dissociative adsorption) and similar corresponding adsorption energies for adsorption of hydrogen on Pd clusters anchored on the vacancies, independently of whether the vacancy was decorated on one side or two sides. In summary, hydrogen is not a successful competitor of palladium to saturate vacancies in the walls of porous carbon materials and therefore the adsorption of hydrogen does not destroy the stability of the palladium doped material. This is important for future hydrogen storage technologies on doped porous carbons.

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##### Notes

The authors declare no competing financial interest.

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#### REFERENCES

- (1) Satyapal, S.; Petrovic, J.; Thomas, G. Gassing up with Hydrogen. *Sci. Am.* **2007**, *296* (4), 80–87.
- (2) Dresselhaus, M. S.; Thomas, I. L. Alternative Energy Technologies. *Nature* **2001**, *414*, 332–337.
- (3) Jena, P. Materials for Hydrogen Storage: Past, Present, and Future. *J. Phys. Chem. Lett.* **2011**, *2*, 206–211.
- (4) Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles September 2009, [http://energy.gov/sites/prod/files/2014/03/f11/targets\\_onboard\\_hydro\\_storage\\_explanation.pdf](http://energy.gov/sites/prod/files/2014/03/f11/targets_onboard_hydro_storage_explanation.pdf) (2009). Last accessed on January 2017.

- (5) Liu, C.; Fan, Y.; Liu, M.; Cong, H.; Cheng, H.; Dresselhaus, M. Hydrogen Storage in Single-Walled Carbon Nanotubes at Room Temperature. *Science* **1999**, *286*, 1127–1129.
- (6) Chen, P.; Wu, X.; Lin, J.; Tan, K. L. High H<sub>2</sub> Uptake by Alkali-Doped Carbon Nanotubes Under Ambient Pressure and Moderate Temperatures. *Science* **1999**, *285*, 91–93.
- (7) Li, J.; Furuta, T.; Goto, H.; Ohashi, T.; Fujiwara, Y.; Yip, S. Theoretical Evaluation of Hydrogen Storage Capacity in Pure Carbon Nanostructures. *J. Chem. Phys.* **2003**, *119*, 2376–2385.
- (8) Bhatia, S. K.; Myers, A. L. Optimum Conditions for Adsorptive Storage. *Langmuir* **2006**, *22*, 1688–1670.
- (9) Contescu, C. I.; Brown, C. M.; Liu, Y.; Bhat, V. V.; Gallego, N. C. Detection of Hydrogen Spillover in Palladium-Modified Activated Carbon Fibers during Hydrogen Adsorption. *J. Phys. Chem. C* **2009**, *113*, 5886–5890.
- (10) Contescu, C. I.; van Benthem, K.; Li, S.; Bonifacio, C. S.; Pennycook, S. J.; Jena, P.; Gallego, N. C. Single Pd Atoms in Activated Carbon Fibers and their Contribution to Hydrogen Storage. *Carbon* **2011**, *49*, 4050–4058.
- (11) Yang, R. T. Hydrogen Storage by Alkali-Doped Carbon Nanotubes-Revisited. *Carbon* **2000**, *38*, 623–626.
- (12) Bhat, V. V.; Contescu, C. I.; Gallego, N. C.; Baker, F. S. Atypical Hydrogen Uptake on Chemically-Activated, Ultramicroporous Carbon. *Carbon* **2010**, *48*, 1331–1340.
- (13) Cabria, I.; López, M. J.; Alonso, J. A. Enhancement of Hydrogen Physisorption on Graphene and Carbon Nanotubes by Li Doping. *J. Chem. Phys.* **2005**, *123*, 204721.
- (14) Cabria, I.; López, M. J.; Alonso, J. A. Hydrogen Storage in Pure and Li-doped Carbon Nanopores: Combined Effects of Concavity and Doping. *J. Chem. Phys.* **2008**, *128*, 144704.
- (15) Tozzini, V.; Pellegrini, V. Prospects for Hydrogen Storage in Graphene. *Phys. Chem. Chem. Phys.* **2013**, *15*, 80–89.
- (16) Parambath, V. B.; Nagar, R.; Sethupathi, K.; Ramaprabhu, S. Investigation of Spillover Mechanism in Palladium Decorated Hydrogen Exfoliated Functionalized Graphene. *J. Phys. Chem. C* **2011**, *115*, 15679–15685.
- (17) Lee, H.; Ihm, J.; Cohen, M.; Louie, S. Calcium-Decorated Graphene-Based Nanostructures for Hydrogen Storage. *Nano Lett.* **2010**, *10*, 793–798.
- (18) Granja, A.; Alonso, J. A.; Cabria, I.; López, M. J. Competition between Molecular and Dissociative Adsorption of Hydrogen on Palladium Clusters Deposited on Defective Graphene. *RSC Adv.* **2015**, *5*, 47945–47953.
- (19) Kubas, G. J. Molecular Hydrogen Complexes: Coordination of a Sigma Bond to Transition Metals. *Acc. Chem. Res.* **1988**, *21*, 120–128.
- (20) Cabria, I.; López, M. J.; Alonso, J. A. Theoretical Study of the Transition from Planar to Three-Dimensional Structures of Palladium Clusters Supported on Graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 035403.
- (21) Sun, Q.; Wang, Q.; Jena, P.; Kawazoe, Y. Clustering of Ti on a C<sub>60</sub> Surface and its Effect on Hydrogen Storage. *J. Am. Chem. Soc.* **2005**, *127*, 14582–14583.
- (22) Krasnov, P. O.; Ding, F.; Singh, A. K.; Yakobson, B. I. Clustering of Sc on SWNT and Reduction of Hydrogen Uptake: Ab-initio All Electron Calculations. *J. Phys. Chem. C* **2007**, *111*, 17977–17980.
- (23) Kim, G.; Jhi, S. H.; Lim, S.; Park, N. Effect of Vacancy Defects in Graphene on Metal Anchoring and Hydrogen Adsorption. *Appl. Phys. Lett.* **2009**, *94*, 173102.
- (24) Lim, D. H.; Negreira, A. S.; Wilcox, J. DFT Studies on the Interaction of Defective Graphene-Supported Fe and Al Nanoparticles. *J. Phys. Chem. C* **2011**, *115*, 8961–8970.
- (25) Fair, K. M.; Cui, X. Y.; Li, L.; Shieh, C. C.; Zheng, R. K.; Liu, Z. W.; Delley, B.; Ford, M. J.; Ringer, S. P.; Stampfl, C. Hydrogen Adsorption Capacity of Adatoms on Double Carbon Vacancies of Graphene: A Trend Study from First Principles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 014102.
- (26) López, M. J.; Cabria, I.; Alonso, J. A. Palladium Clusters Anchored on Graphene Vacancies and Their Effect on the Reversible Adsorption of Hydrogen. *J. Phys. Chem. C* **2014**, *118*, 5081–5090.
- (27) Cabria, I.; López, M. J.; Fraile, S.; Alonso, J. A. Adsorption and Dissociation of Molecular Hydrogen on Palladium Clusters Supported on Graphene. *J. Phys. Chem. C* **2012**, *116*, 21179–21189.
- (28) Ramos-Castillo, C. M.; Reveles, J. U.; Zope, R. R.; de Coss, R. Palladium Clusters Supported on Graphene Monovacancies for Hydrogen Storage. *J. Phys. Chem. C* **2015**, *119*, 8402–8409.
- (29) Pelzer, A. W.; Jellinek, J.; Jackson, K. H<sub>2</sub> Saturation on Palladium Clusters. *J. Phys. Chem. A* **2015**, *119*, 3594–3603.
- (30) Granja-DelRío, A.; Alonso, J. A.; López, M. J. Steric and Chemical Effects on the Hydrogen Adsorption and Dissociation on Free and Graphene-Supported Palladium Clusters. *Computational and Theoretical Chemistry* **2016**, DOI: 10.1016/j.comptc.2016.11.029.
- (31) Seenithurai, S.; Pandyan, R. K.; Kumar, S. V.; Saranya, C.; Mahendran, M. Li-Decorated Double Vacancy Graphene for Hydrogen Storage Application: A First Principles Study. *Int. J. Hydrogen Energy* **2014**, *39*, 11016–11026.
- (32) Ao, Z.; Dou, S.; Xu, Z.; Jiang, Q.; Wang, G. Hydrogen Storage in Porous Graphene with Al Decoration. *Int. J. Hydrogen Energy* **2014**, *39*, 16244–16251.
- (33) Yadav, S.; Zhu, Z.; Singh, C. V. Defect Engineering of Graphene for Effective Hydrogen Storage. *Int. J. Hydrogen Energy* **2014**, *39*, 4981–4995.
- (34) Rangel, E.; Sansores, E.; Vallejo, E.; Hernández-Hernández, A.; López-Pérez, P. A. Study of the Interplay Between N-Graphene Defects and Small Pd Clusters for Enhanced Hydrogen Storage Via a Spillover Mechanism. *Phys. Chem. Chem. Phys.* **2016**, *18*, 33158–33170.
- (35) dacapo, dacapo: See <https://wiki.fysik.dtu.dk/dacapo> for a description of the total energy code, based on the density functional theory (2009). Last accessed on January 2017.
- (36) Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, *41*, R7892–7895.
- (37) Monkhorst, H.; Pack, J. Special Points for Brillouin-Zone Integration. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (38) Perdew, J. P.; Wang, Y. Accurate and Simple Analytic Representation of the Electron-Gas Correlation Energy. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *45*, 13244–13249.
- (39) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and Accurate ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (40) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (41) Smith, D. G. A.; Burns, L. A.; Patkowski, K.; Sherrill, C. D. Revised Damping Parameters for the D3 Dispersion Correction to Density Functional Theory. *J. Phys. Chem. Lett.* **2016**, *7*, 2197–2203.
- (42) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (43) Bores, C.; Cabria, I.; Alonso, J. A.; López, M. J. Adsorption and Dissociation of Molecular Hydrogen on the Edges of Graphene Nanoribbons. *J. Nanopart. Res.* **2012**, *14*, 1263.
- (44) Jiang, Q. G.; Ao, Z. M.; Zheng, W. T.; Li, S.; Jiang, Q. Enhanced Hydrogen Sensing Properties of Graphene by Introducing a Mono-Atom-Vacancy. *Phys. Chem. Chem. Phys.* **2013**, *15*, 21016–21022.