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ABSTRACT

Hydrogen technology is set to be a key energy alternative for mitigating pollution and reducing CO₂ emissions. However, the current storage mechanism of hydrogen molecules in carbon fiber tanks detracts from the fuel economy of hydrogen in mobile applications, necessitating the development of alternative storage mechanisms. Adsorbing hydrogen in its molecular form (H₂) under typical operating conditions of proton exchange membranes can potentially meet storage requirements. However, H₂ is the smallest molecule with only two electrons and, therefore, it has very limited propensity to physisorb in a material within the binding energy window of -0.2 to -0.4 eV that is suitable for storage. Calcium atom decorators on graphene have previously shown promise for tunable H₂ binding, but the system is thermodynamically unstable toward the formation of calcium hydride. Moreover, the absolute adsorption of H₂ is challenging to predict accurately and is typically overestimated with van der Waals inclusive density functional approximations. In this work, we perform *state-of-the-art* fixed-node diffusion Monte Carlo alongside a selection of density functional approximations for two strategies of anchoring Ca: (i) Ca on boron-doped graphene and (ii) Ca inside carbon nanotubes. We predict reliable Ca and H₂ binding energies and establish that Ca is anchored inside carbon nanotubes and on boron-doped graphene, while boosting the H₂ adsorption energy. Importantly, the H₂ adsorption energy is found to be improved by the anchoring strategies, with the energy inside a Ca decorated carbon nanotube reaching the viable storage window. The reference DMC binding energies provide much-needed benchmarks for developing data-driven methods and guiding experiment in the systematic design of hydrogen storage materials.

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I. INTRODUCTION

H₂ technology is one of the key strategies for mitigating greenhouse gas emissions as H₂ molecules are converted into energy and water using proton exchange membranes (PEMs), delivering a high energy density with no local CO₂ emissions. However, novel storage materials are needed to propel H₂ technology, particularly for mobile applications. Currently, expensive carbon fiber tanks are used to contain pressurized H₂ gas up to ~ 700 bars.^{1,2} Pressurizing H₂ to this extent is an energy intensive process and detracts significantly from the energy efficiency of using H₂. Alternative lower pressure storage solutions are sought to improve the energy efficiency of using H₂ and minimize the cost of storage. To this end, the adsorption energy of H₂ molecules plays a major role in the

viability of H₂ storage materials. Strong dissociative adsorption of H₂ produces adsorbed H atoms, so substantial energy is required for their recombination and desorption as H₂ for use in PEMs. Instead, adsorbing molecular H₂ in an energy window of approximately -0.2 to -0.4 eV per H₂ molecule in low-dimensional materials has been theorized to correspond to the operating conditions of a typical PEM.^{3–5}

The challenge for meeting the target adsorption energy window for H₂ lies in its small, two-electron, and non-polar nature. Many studies, especially using density functional theory (DFT), have focused on this challenge, with some applying a high-throughput approach to tackle the many thousands of low-dimensional materials being synthesized or hypothesized^{6–9} and others applying a bottom-up approach focusing on the mechanistic details.^{3,10–19} In

our previous work, we applied the latter approach and also reported beyond-DFT adsorption energies for a selection of group 1 and group 2 metal decorated graphene substrates.^{3,18,19} It has been shown that group 1 metal adatoms boost the H₂ adsorption energy well beyond the weak adsorption on pristine graphene, through static polarization.³ This form of interaction is weakened with each additional H₂ molecule and group 1 metal decorated graphene is, therefore, at the edge of being a useful storage material. On the other hand, Ca and Sr decorated graphene has been shown to facilitate the adsorption of multiple H₂ molecules through a weak covalent interaction known as Kubas bonding.^{3,20,21} This form of bonding is only exhibited where an occupied metal d-state is available to overlap with the anti-bonding H₂ 1σ* state. However, due to the intricate balance of physical interactions, including long-range dispersion forces, static polarization, charge transfer, and weak covalent bonding, the H₂ adsorption energy is very sensitive to the computational method that is applied and in particular to the delocalization error in density functional approximations (DFAs).²² Meanwhile, state-of-the-art diffusion Monte Carlo (DMC) is a wavefunction-based method that is free of the delocalization error and accounts for full many-body dispersion interactions. DMC adsorption energies are, therefore, accurate references that can be used as a guide in DFT modeling to arrive at reliable insights. For example, we have shown using DMC that Kubas binding H₂ is feasible on Ca-decorated graphene.¹⁹

An important current challenge is to ensure the stability of the single atom Ca decorator. It has previously been shown that Ca has a low barrier to diffuse across the graphene surface and that the system is unstable toward the formation of calcium hydride and graphite.^{3,23} Several strategies previously been considered for anchoring Ca adatoms and two mechanisms that we consider here are (i) to increase the Ca-substrate interaction through boron doping of graphene, and (ii) to increase the physical barrier for Ca to agglomerate by adsorbing inside carbon nanotubes (CNTs). First, boron doping in graphene reduces the electron density relative to pristine graphene and, therefore, strengthens the electron transfer from Ca to the surface. Second, CNTs typically adsorb atoms and molecules more strongly than pristine graphene¹⁸ and thanks to their lower dimensionality, CNTs have a more closed structure that is expected to help segregate adatoms such as Ca. Given the difficulty of accurately capturing the H₂ interaction, we apply a selection of widely used and well-performing DFAs alongside DMC, to predict the anchoring of Ca adatoms and the impact of these strategies on H₂ adsorption. In the following, we detail the system setup and computational methods in Sec. II; we report the results for Ca decorated BGr in Sec. III A and for Ca decorated CNTs in Sec. III B. We provide a brief discussion in Sec. IV and conclude in Sec. V.

II. METHODS

A. System setup

The boron-doped graphene (BGr) system is made by the substitution of a single carbon atom in a (5 × 5) unit cell of graphene, with a 20.0 Å vacuum in the direction perpendicular to the sheet, as shown in Fig. 1. CNT-based systems have a vacuum of 10.0 Å in perpendicular directions to the CNT and approximate length of 8.5 Å. Structures can be found in the [supplementary material](#). The binding energy ($E_b^{H_2}$) of a hydrogen molecule is computed as

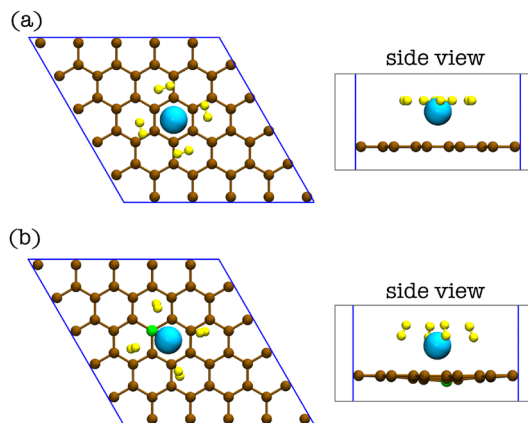


FIG. 1. Configurations for 4H₂ adsorption on 2D materials, with H atoms indicated in yellow, Ca indicated in blue, C indicated in brown, and B indicated in green: (a) Ca decorated graphene (Ca@Gr) and (b) Ca decorated B-doped graphene (Ca@BGr). The configurations are obtained from PBE+D3 geometry optimizations.

$$E_b^{H_2} = (E_{nH_2+substrate} - E_{substrate} - nE_{H_2})/n, \quad (1)$$

where $E_{nH_2+substrate}$ is the total energy of n H₂ molecules adsorbed on a substrate, $E_{substrate}$ is the total energy of a substrate, and E_{H_2} is the total energy of an isolated H₂ molecule in the gas phase. The substrate system includes Ca, where present, for computing $E_b^{H_2}$. The binding energy of a Ca adatom, E_b^{Ca} , is computed as

$$E_b^{Ca} = E_{Ca+substrate} - E_{substrate} - E_{Ca}, \quad (2)$$

where E_{Ca} is total energy of an isolated Ca atom in the gas phase. Each system is fully relaxed using PBE+D3^{24,25} and a consistent unit cell is used across all terms for each binding energy.

The binding energies reported in this work are fixed-nuclei electronic energies. Zero-point, entropic, and finite-temperature free-energy contributions are not included, so the values should be interpreted as electronic benchmarks rather than adsorption enthalpies or finite-temperature storage free energies.

The QMC calculations use one substitutional B atom in a 5 × 5 graphene supercell, corresponding to a B concentration of 2.0%. Since Ca adsorption on graphene is charge-transfer mediated, the periodic repetition of Ca@BGr units may also introduce electrostatic finite-concentration effects associated with the charge redistribution and dipole of the adsorbed Ca-substrate complex. To assess the sensitivity of the results to this finite concentration, we performed additional fixed-geometry PBE calculations in larger $N \times N$ cells, with $N = 6-10$. These tests, reported in Sec. S4 of the [supplementary material](#), show that reducing the B concentration down to 0.5% changes the H₂ adsorption energy by at most ~24 meV/H₂ and the Ca adsorption energy by at most ~19 meV. We, therefore, expect finite-concentration effects to be modest for the qualitative conclusions of this benchmark, while noting that the DMC results refer to the finite 5 × 5 periodic model rather than to a fully extrapolated dilute limit.

B. Structure search

The potential energy surface is typically shallow for physisorbed H_2 molecules and, therefore, a random structure search was used to generate 50 configurations of H_2 in the CNT(10,0) substrate and optimized with PBE+D3^{24,25} and the CP2K code.²⁶ The initial H_2 molecules were generated to be within 3.5 Å of the Ca atom and on the inside of the CNT, with random orientation. The absolute energy difference among the 20 lowest energy structures was less than ~15 meV. Ten lowest energy structures were optimized using the numerical settings in VASP v.6.2.1^{27–29} given in Sec. II C. The lowest energy Ca– H_2 configuration in CNT(10,0) was used as the starting geometry for CNT(8,0), CNT(5,5), and CNT(6,6).

We geometry optimized Ca at symmetrically distinct rings on the surface of BGr to find the lowest energy adsorption site as well as starting with atom-top initial configurations. The lowest energy configuration has Ca on the BC_5 ring, with Ca shifted toward B. Similarly, we geometry optimized upright, flat, and radial orientations of one and four H_2 molecules around the Ca atom on BGr (on the lowest-energy Ca@BGr structure) to find the lowest energy configuration. The adsorption of 4 H_2 molecules does not change the site of Ca adsorption on BGr, and the final 4 H_2 +Ca@BGr geometry can be seen in Fig. 1.

C. DFT setup

Standard PAW potentials^{30,31} are used in the VASP v.6.2.1 code, with a 500 eV plane-wave cutoff and the configurations have been optimized with PBE+D3 (zero damping and no three-body ATM terms) to forces smaller than 0.005 eV Å^{−1}, and an energy criterion of 10^{−6} eV. A 9 × 9 × 1 and a 1 × 1 × 7 Γ centered $\mathbf{k}$ -point grid are used in DFT calculations for the 2d and 1d systems, respectively. Gas phase H_2 and Ca energies are computed in the corresponding unit cells for each binding energy calculation. $E_b^{\text{H}_2}$ is converged to within 1 meV at the chosen $\mathbf{k}$ -point grids with respect to fully converged grids. The lowest energy structure found with PBE+D3 for each system is fixed for subsequent benchmarking with a selection of DFAs (optB86b-vdW,³² r2SCAN,³³ r2SCAN+rVV10,^{33,34} PBE+MBD,^{24,35,36} PBE+MBD-FI,^{24,37,38} rev-vdW-DF2,³⁹ PBE, and the LDA) and DMC.

D. QMC setup

We used Quantum Espresso v6.8^{40,41} to compute the LDA orbitals as input for single Slater determinant QMC computations in the QMCPACK (v.3.9) code.⁴² Non-spin polarized LDA orbitals were computed using 400 Ry plane-wave cutoffs in combination with ccECP potentials for H, Ca, C, and B atoms.⁴³ The planewave orbitals were localized using B-splines⁴⁴ and a mesh factor of 0.5 in QMCPACK. This setup, and in particular the use of LDA orbitals, is consistent with previous studies.^{18,19} Although the choice of orbitals can affect the total energy through the fixed-node approximation, interaction energies are expected to benefit from partial cancellation of fixed-node errors. This was observed, for instance, in a proxy system for the present problem, namely, the gas-phase 4 H_2 +Ca⁺ cluster, for which LDA and B3LYP orbitals yielded nearly indistinguishable interaction energies.¹⁹ For a more efficient Brillouin sampling, we used a special twist on to the 2 × 2 supercell. Full

details of the QMC twists and supercells used can be found in the [supplementary material](#). The spin polarization contribution was estimated at the LDA level for BGr-based systems. There is no spin-polarization contribution to the CNT(6,6)-based systems. One- and two-body Jastrow factors have been optimized for all systems using the OneShiftOnly algorithm, as implemented in QMCPACK. The determinant localization approximation^{45,46} and the ZSGMA branching scheme⁴⁷ were used for all DMC calculations along with a careful time step convergence (see the [supplementary material](#)). The QMC calculations are prone to finite-size effects that stem from explicit electrons and this has been estimated at the DFT level with the KZK correction.⁴⁸ Numerical details can be found in the [supplementary material](#) while we report DMC values that carry the smallest KZK corrections in Sec. III. The workflows were managed by the NEXUS python package.⁴⁹

III. RESULTS

A. Adsorbing multiple H_2 molecules on Ca decorated boron-doped graphene

We have previously found that the adsorption of H_2 on pristine graphene is very weak, at -20 ± 3 meV from DMC.¹⁹ We also found that decorating pristine graphene with Ca boosts the H_2 binding energy by ~90 meV.¹⁹ While this is still outside of the viable binding energy window for H_2 storage, the bonding mechanism involves a Ca 3d to H_2 1σ* (Kubas) interaction, which makes it energetically favorable to bind four H_2 molecules due to the symmetry of the states. This is different to static polarizable adsorption of H_2 , as exhibited by group 1 metal decorated graphene, e.g., Li@Gr and Na@Gr, where the maximal binding energy occurs for the first H_2 molecule and it decreases for each additional H_2 .³ However, Ca has a low barrier to diffuse across pristine graphene, and previous studies indicate that it is thermodynamically unstable toward the formation of calcium hydride and graphite in the presence of H_2 .²³ First, we report the binding energy of Ca on boron-doped graphene (Ca@BGr) to establish whether boron doping makes Ca adsorb on graphene more strongly. Second, we predict the adsorption energy of 4 H_2 +Ca@BGr with a selection of widely used DFAs and DMC to understand the impact on the H_2 interaction.

We can see from Fig. 2 that B doping graphene substantially strengthens the adsorption of Ca on the substrate. An increase of ~1.5 eV in the Ca adsorption strength is predicted consistently by all of the electronic structure methods that we apply, including DMC. Furthermore, we computed the PBE+D3 energy barrier for the diffusion of Ca to the nearest carbon-only ring in the surface, using the nudged-elastic-band (NEB) method (full details are given in the [supplementary material](#)). On pristine graphene, the Ca diffusion barrier was previously found to be 0.13 eV using the same methodology.³ We find here that there is a monotonic energy increase of 0.28 eV for the Ca to reach the carbon-only ring in BGr, indicating an improvement in the localization of the Ca adatom. The indication on the whole is that increased stability is brought by the markedly stronger binding energy of Ca on BGr. Our findings support the use of BGr for anchoring Ca atoms and are consistent with a charge-transfer-mediated picture of Ca adsorption: substitutional B locally increases the electron-accepting character of the graphene sheet, strengthening the Ca–substrate interaction and localizing the Ca adatom near the BC_5 ring. A similar effect can be expected for

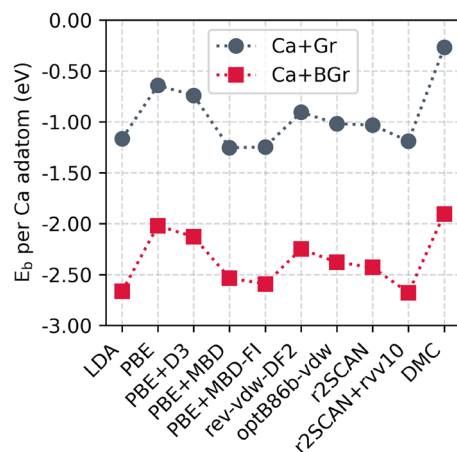


FIG. 2. Binding energy of Ca on graphene represented in gray and B-doped graphene represented in red, across a selection of DFAs and DMC.

other metal adatoms where the metal–substrate binding is charge-transfer-mediated. It is noteworthy that for Ca@Gr, the DFAs we consider overestimate the adsorption of Ca by ~ 0.5 eV. Meanwhile, there is much better agreement for Ca@BGr with PBE and PBE+D3 (within ~ 0.3 eV of the DMC reference). It can also be seen that adding explicit dispersion corrections to PBE or r2SCAN does not necessarily improve agreement with the DMC benchmark. Neither does this imply that dispersion is unimportant nor does it provide a direct diagnostic of delocalization error alone. Although r2SCAN is expected to reduce several semilocal functional errors relative to PBE, the adsorption energy in these systems results from a balance of long-range dispersion, polarization, charge transfer, medium-range correlation, and metal–adsorbate interactions. Delocalization/self-interaction errors in the parent semilocal functional are, therefore, plausible contributors to the observed overbinding, but they are not the only possible source of error. If the parent functional is already too attractive, an additional attractive dispersion term can increase the net overbinding and move the result further from DMC.

Having established that Ca is strongly adsorbed on BGr, we consider the adsorption of four H_2 molecules on Ca@BGr. The adsorption motif was optimized with the PBE+D3 functional and fixed for all other electronic structure methods that we apply. This is necessary in order to compare the interaction strengths with DMC, for which it is not feasible to optimize the geometry. For context, we also report the H_2 adsorption energy on pristine graphene (H_2 +Gr) and $4H_2$ +Ca@Gr shown in Fig. 3 from previous work.¹⁹ We compute these systems here with the same selection of DFAs and settings as given in Sec. II for consistency. It is evident that pristine graphene can only very weakly physisorb a H_2 molecule and it would not be a viable storage material on its own, while introducing a Ca adatom that boosts the H_2 interaction by ~ 100 meV. Moreover, it has previously been established that H_2 is bound via Kubas bonding on Ca decorated graphene, such that four H_2 molecules are adsorbed around a Ca atom. While anchoring Ca with B doping, it can be seen from Fig. 3 that DMC and all DFAs considered, with the exception of LDA, predict a weak boost of 10–20 meV in adsorption strength per H_2 molecule. Therefore, B doping graphene can be used

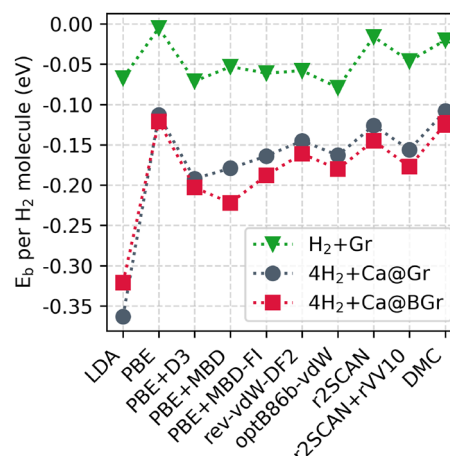


FIG. 3. Binding energy of $4H_2$ per H_2 molecule on Ca@Gr represented in gray and Ca@BGr represented in red, across a selection of DFAs and DMC. The binding energy of a single H_2 molecule on pristine graphene is also represented with the green triangles.

to stabilize Ca adatoms without deteriorating the H_2 adsorption. The consistency among GGA and *meta*-GGA functionals for the order of adsorption on Ca@Gr and Ca@BGr surfaces is a positive indication for the use of these methods, although the predicted H_2 adsorption energy varies by up to ~ 70 meV even among DFAs that account for some dispersion interactions. Indeed, PBE+D3 and PBE+MBD predictions fall marginally within the viable window of binding energy for H_2 storage, but without a reference, it would not be possible to ascertain which prediction is best. Thanks to the DMC reference, it can be seen that PBE, r2SCAN, and rev-vdW-DF2 predict the most accurate adsorption energies. Although PBE and r2SCAN are among the closest to DMC for this fixed-geometry adsorption energy, they do not include an explicit description of long-range dispersion. We, therefore, regard rev-vdW-DF2, which includes nonlocal correlation while retaining good agreement with the DMC benchmark, as the more physically motivated choice among the DFAs tested here.

B. Viable H_2 binding strength in Ca decorated carbon nanotubes

Carbon nanotubes (CNTs) are readily synthesized materials, and their two key characteristics are the tube diameter and chirality, which together determine the electronic character of the tube. In the present work, we consider both armchair CNTs, CNT(5,5), and CNT(6,6), which are metallic, and zigzag CNTs, CNT(8,0), and CNT(10,0), which are semiconducting. There has been a longstanding interest in exploiting the open structure of CNTs for gas storage but the controlled synthesis of specific CNTs remains an experimentally challenging process. It is, therefore, useful to gain insight from computational modeling on the effect of the CNT diameter and electronic state on the adsorption energy of H_2 . Many previous studies have focused on this for clean and unmodified CNTs, showing that H_2 generally binds most effectively in CNTs with a diameter of 7–10 Å, irrespective of whether a metallic or semi-conducting CNT is used.^{50–55} We have previously shown using DMC that the interaction energy of H_2 inside a semi-conducting CNT(10,0) with

7.8 Å diameter is -115 ± 11 meV.¹⁸ This is considerably stronger than binding on pristine graphene but still weaker than the ideal binding energy window for H₂ storage. Moreover, many widely used DFAs were shown to overestimate H₂ adsorption inside the CNT due to the accumulation of errors in medium-range electron correlation. This source of inaccuracy can be expected for any molecule under confinement and, therefore, makes it difficult to rely on a DFA without a reliable reference of the adsorption energy.

Here, we computed the DMC adsorption energy for a H₂ molecule inside a Ca decorated armchair CNT(6,6), shown in Fig. 4, alongside a selection of widely used DFAs. Note that CNT(6,6) has a diameter only ~ 0.3 Å larger than CNT(10,0), but it has a different chirality and electronic structure, and CNT(6,6) is non-spin

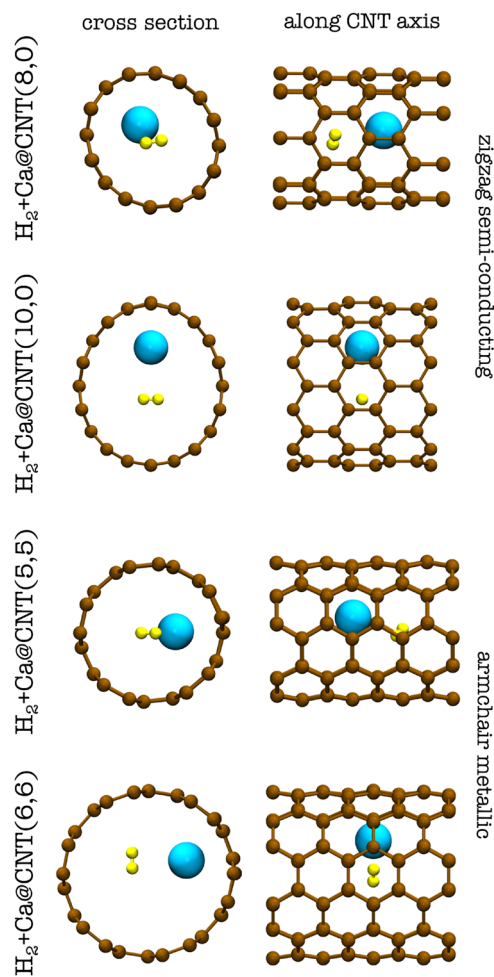


FIG. 4. H₂+Ca@CNT configurations obtained from RSS and PBE+D3 geometry optimizations. From the top: zigzag semi-conducting CNTs (8,0) and (10,0) with diameters of 6.26 and 7.83 Å, respectively, and armchair metallic CNTs (5,5) and (6,6) with diameters of 6.74 and 8.14 Å, respectively. All configurations are treated in full periodic boundary conditions (unit cell boundaries not shown) with a vacuum of 10.0 Å perpendicular to the CNT tube axis and the nearest Ca–Ca distance along the CNT axis is 8.5 Å. H atoms are represented by yellow, C by brown, and Ca by blue.

polarized upon the adsorption of Ca, unlike CNT(10,0). As such, it is more memory-efficient to compute the wavefunction for H₂ molecule in Ca@CNT(6,6) with DMC. Note that the LDA, PBE, PBE+D3, and PBE+MBD H₂ binding energies in pristine CNT(10,0) reported previously¹⁸ are within 10 meV of the corresponding binding energies in CNT(6,6). Assuming a similar consistency at the DMC level, the DMC H₂ binding energy for pristine CNT(10,0) and Ca@CNT(6,6), as shown in Fig. 5, gives an approximate indication about the effect of Ca decoration from DMC. However, we consider the previously reported DMC value for pristine CNT(10,0) only as a qualitative reference for H₂ adsorption in an undecorated CNT of similar diameter, rather than as a strict quantitative reference for pristine CNT(6,6). The DMC result for Ca@CNT(6,6) is then used to assess whether the DFT picture of enhanced H₂ adsorption upon Ca decoration is qualitatively supported at the many-body level. It can be seen from Fig. 5 that H₂ binding is boosted by over 100 meV inside Ca@CNT(6,6) relative to pristine CNT(6,6) according to all the methods we consider.

The Ca binding energy inside CNTs can be seen in Fig. 6. The Ca binding energy is weaker for larger CNT diameters, which is expected as the Ca binding energy tends toward the Ca@Gr binding energy with reduced curvature of the CNT. Figure 6 also shows that the DFA predictions lie in a remarkably large range of ~ 1 eV, indicating a large error in the absolute interaction strength. However, it can be seen that the deviations are systematic, such that the overall trend is consistent across the CNTs considered. In particular, all DFAs we apply predict the strength of Ca binding as CNT(8,0) > CNT(5,5) $\approx$ CNT(10,0) > CNT(6,6). Within the present set of nanotubes, the metallic armchair CNTs, CNT(5,5) and CNT(6,6), are found to adsorb Ca more weakly than the semiconducting zigzag CNTs, CNT(8,0) and CNT(10,0), for similar CNT diameters. On the

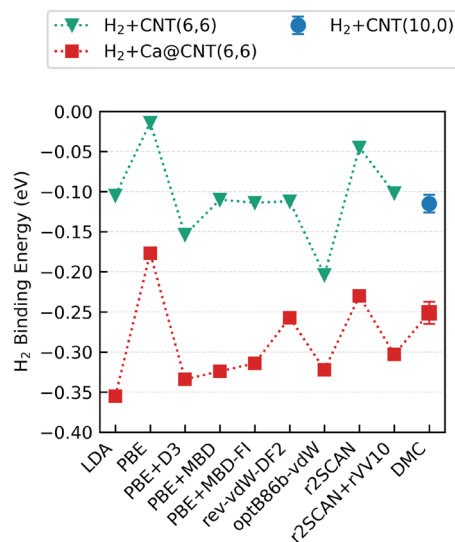


FIG. 5. H₂ binding energy with a selection of DFAs inside pristine CNT(6,6) indicated by the green triangles and inside Ca decorated CNT(6,6) indicated by the red squares. The DMC binding energy of H₂ inside pristine CNT(10,0) from Ref. 18 is represented with a blue circle as a qualitative reference for an undecorated CNT of similar diameter.

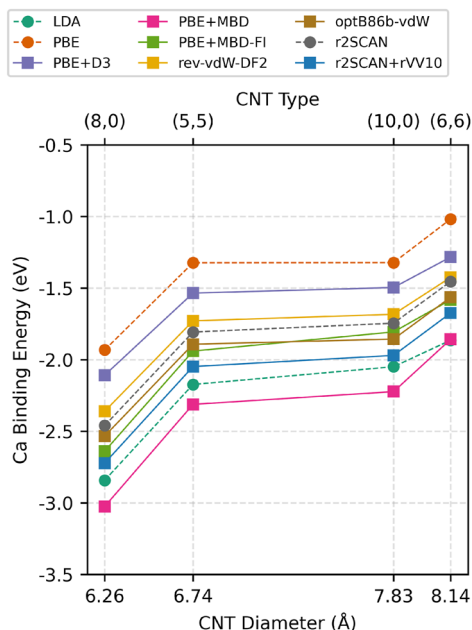


FIG. 6. Ca interaction energy inside CNTs is in units of eV. The chirality and diameter of the CNTs are indicated on the top and bottom x axes, respectively. LDA, PBE, and r2SCAN are indicated with circles and dashed lines to distinguish them as methods not including approximations for long-range correlation.

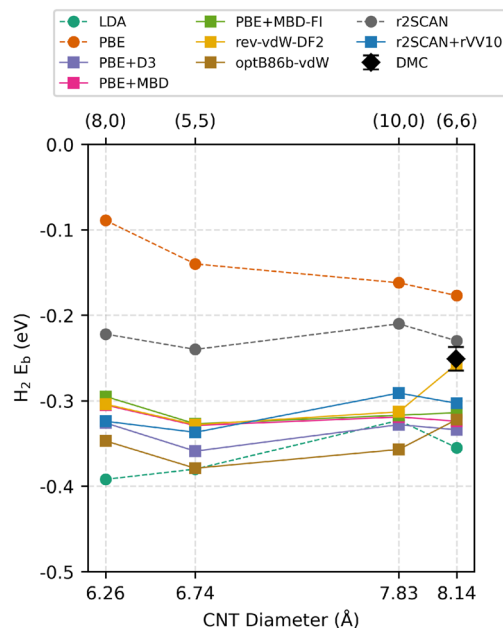


FIG. 7. H₂ interaction energy inside Ca@CNT systems is in units of eV. The chirality and diameter of the CNTs are indicated on the top and bottom x axes, respectively. LDA, PBE, and r2SCAN are indicated with circles and dashed lines to distinguish them as methods not including approximations for long-range correlation.

whole, the Ca+CNT binding energy is relatively strong, and given the structural barriers to agglomeration, CNTs can be considered as an anchoring substrate for Ca adatoms.

The H₂ interaction strength is predicted to be within -0.2 to -0.4 eV across all Ca@CNT systems considered here with all DFAs applied, aside from PBE. However, previous work has shown that non-local correlation has a notable impact on the H₂ binding energy inside CNTs and that such configurations are susceptible to being overestimated as a result of accumulated errors in the medium-range correlation energy.¹⁸ Here, we report the reference DMC interaction strength for H₂+Ca@CNT(6,6) at the PBE+D3 geometry. This can be seen from Fig. 7 to be within the binding energy window of H₂ storage, at -251 ± 14 meV. As such, Ca decorated CNTs can be considered promising materials for H₂ storage.

It can be seen from Fig. 7 that rev-vdW-DF2 and r2SCAN interaction strengths agree remarkably well with DMC and yield typically weaker adsorption than the other DFAs that account for non-local correlation. Given that the geometry is fixed to be the same across all of the methods reported, we also considered the impact of optimizing each configuration for each DFA. We find that there is negligible change in the adsorption energies and structures, cementing the validity of the PBE+D3 optimized configurations and the performance of the methods (see the [supplementary material](#)). We also note that rev-vdW-DF2 and optB86b-vdW, which are both density-dependent vdW-inclusive DFAs, predict a weaker adsorption on Ca@CNT(6,6) than on Ca@CNT(10,0), in contrast to the other DFAs considered. This suggests that the density-dependent vdW DFAs are more sensitive to the electronic structure of the CNT,

and this can be important, for example, in developing data-driven methods with training data from DFAs.

IV. DISCUSSION

The DMC reference adsorption energies reported here show that many DFAs overbind H₂ in these Ca-decorated low-dimensional systems. Consequently, adding an explicit attractive dispersion correction to a semilocal functional does not automatically improve the total adsorption energy. Dispersion is physically important, but the net DFA error also contains contributions from delocalization/self-interaction, charge transfer, polarization, and medium-range correlation. When these errors already make the parent functional too attractive, the added dispersion contribution can lead to further overbinding. Hybrid functionals could help assess the role of delocalization/self-interaction error more directly, for example, by modifying the degree of Ca-substrate charge transfer, but we do not expect them to change the qualitative trends established here, which are consistent across the DFAs tested and supported by DMC. Isolated Ca-H₂ or Ca-(H₂)₄ clusters are useful references for the local metal-H₂ interaction,^{19,22} but they do not fully represent the supported systems studied here. The substrate changes the charge state, polarization, and electronic structure of Ca and also contributes directly to H₂ binding through dispersion and medium-range correlation. Thus, the DFA error should be viewed as a coupled Ca-substrate, Ca-H₂, and substrate-H₂ error, rather than as an isolated Ca-H₂ error alone. In general, the selection of DFAs we consider exhibits mostly systematic shifts in the absolute adsorption energies of Ca and H₂. However, a difference in trend is found

between CNT(10,0) and CNT(6,6) for rev-vdW-DF2 and optB86b-vdW against other DFAs, indicating a sensitivity to the underlying electronic structure of the zigzag and armchair nanotubes. Given the DMC reference energies reported in this work and the importance of long-range dispersion interactions in low-dimensional substrates, the rev-vdW-DF2 method is found to perform relatively well across the systems considered.

With the DMC adsorption references reported in this work, it can be seen that DFAs that were typically applied in previous studies, such as the LDA or PBE functionals, yield quantitatively unreliable but qualitatively reasonable results.

For quantitative comparison with experiment or with operating-temperature storage performance, vibrational and finite-temperature contributions would also be required. These effects can be comparable with some of the smaller electronic energy differences discussed here, and their role in connecting H_2 adsorption energies to temperature and pressure conditions has been discussed previously for metal-decorated graphene.³ The present work, therefore, focuses on benchmarking fixed-geometry electronic adsorption energies from DMC and DFT.

We have reliably cemented the role of B in anchoring a Ca adatom by ~ 1.5 eV relative to pristine graphene. In addition, Ca boosts the adsorption of H_2 on the order of ~ 100 meV relative to undecorated low-dimensional carbon materials. The H_2 adsorption interaction arises from a combination of attractive long-range dispersion between the molecule and the substrate, polarization and charge-transfer effects, and the local Kubas-type interaction with the Ca adatom. The importance of dispersion can be deduced from the net D3, MBD, MBD-FI, and rVV10 dispersion contributions in the systems considered here; these indicate that 20%–40% of the total interaction energy is long-range dispersion. Therefore, prospective efforts to find a suitable H_2 storage material should focus on maximizing these two interactions. For example, a plethora of covalent organic frameworks have been synthesized or hypothesized, which may provide a framework with higher polarizability for stronger dispersion interactions. Meanwhile, the Kubas interaction may be optimized further by considering other metal decorators such as light transition metals. The synthesis and control of single metal atom decorated low-dimensional materials remains a considerable experimental challenge,⁹ but Ca-decorated graphene, for example, has been successfully synthesized using at least two different methods.^{56–58} The work presented here serves as an indication of the promising potential in these materials and support for continued efforts.

V. CONCLUSION

H_2 molecule and Ca adatom adsorption has been reported for a selection of low-dimensional carbon allotropes (graphene and CNT based). We applied a selection of widely used and recently developed DFAs as well as *state-of-the-art* DMC to deliver robust insights. DMC and DFT methods show that boron doping in graphene (BGr) stabilizes Ca adsorption by over 1 eV compared to pristine graphene. Importantly, a small boost of 10–20 meV per H_2 is found in $4H_2 + Ca@BGr$, relative to $4H_2 + Ca@Gr$, indicating that the B aided anchoring of Ca does not deteriorate the adsorption of H_2 molecules and even slightly improves it. Graphene functionalized in this way makes a significant step toward the goal of

obtaining adsorption energies in the range of -200 to -400 meV for viable hydrogen storage. We also computed H_2 binding in Ca-decorated CNTs. Previous DMC work found that H_2 binds inside pristine CNT(10,0) with an adsorption energy of -115 ± 11 meV, while here we report a DMC adsorption energy of -251 ± 14 meV for $H_2 + Ca@CNT(6,6)$. Because these two DMC values correspond to CNTs with similar diameter but different chirality and decoration, they should be viewed as a qualitative comparison. Nevertheless, the DMC result for $Ca@CNT(6,6)$ supports the DFT picture that Ca decoration substantially strengthens H_2 adsorption and can bring the fixed-nuclei electronic adsorption energy into the range commonly associated with viable molecular hydrogen storage. Moreover, the Ca binding energy inside CNTs with diameters of 6–8 Å is stronger than -1 eV while the CNTs are expected to structurally inhibit Ca agglomeration.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional computational details and numerical tests. The [supplementary material](#) includes DMC time step convergence tests, spin-polarization and finite-size corrections for the QMC calculations, details of the Ca diffusion barrier calculations on B-doped graphene, optimized CNT structures obtained with different density functional approximations, and fixed-geometry finite-concentration tests for B-doped graphene.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yasmine S. Al-Hamdani: Conceptualization (supporting); Data curation (lead); Formal analysis (lead); Investigation (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal). **Dario Alfè:** Conceptualization (equal); Funding

acquisition (supporting); Investigation (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal). **Andrea Zen:** Conceptualization (equal); Formal analysis (supporting); Funding acquisition (lead); Investigation (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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