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Sodium decorated net-Y nanosheet for hydrogen storage and adsorption mechanism: A first-principles study*

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Using first-principles calculations based on density functional theory (DFT), we investigate the potential hydrogen storage capacity of the Na-decorated net-Y single layer nanosheet. For double-side Na decoration, the average binding energy is 1.54 eV, which is much larger than the cohesive energy of 1.13 eV for bulk Na. A maximum of four H_2 molecules can be adsorbed around each Na with average adsorption energies of 0.25–0.32 eV/H_2. Also, H_2 storage gravimetric of 8.85 wt% is obtained, and this meets the U.S. Department of Energy (DOE) ultimate target. These results are instrumental in seeking a promising hydrogen energy carrier.

Keywords: hydrogen storage, net-Y, storage gravimetric, density functional theory

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1. Introduction

Energy shortages and environment problems have become the theme of global energy problems with the depletion of fossil fuels. From the perspective of future social energy structures, humans face the problems of increasing depletion of coal, oil, and other mineral energy sources on the one hand, and face problems of environmental pollution that are caused by mineral energy sources on the other hand. Therefore, the quest for new energy alternatives to traditional hydrocarbon energy should be one of the very highest priorities for sustainable development. Hydrogen energy is notable because it has pollution-free characteristics, a high combustion value, and extensive resources.[1,2] In these regards, hydrogen storage is crucial for industrial applications of hydrogen energy. However, there are still many problems that must be solved, such as lower hydrogen adsorption capacity and desorption with bad reversible behavior.[3,4] The latest hydrogen storage goals that have been set by the U.S. Department of Energy (DOE) include a gravimetric density of 4.5 wt% and a volumetric density of 30 g/L at ambient temperature and under appropriate pressure by 2020.[5] In addition, the binding energy of hydrogen to carbon materials should be maintained in the range of ∼0.2–0.4 eV per hydrogen molecule for the reversible hydrogen adsorption or desorption under realistic conditions.[6] Innumerable scientists have dedicated themselves to exploring feasible materials that meet the targets for both gravimetric and volumetric capacity. Various templates have been reported one after another, including metal/nonmetal hydrides,[7–12] formic acid,[13,14] carbon materials,[15–19] other noncarbon systems,[20–22] covalent-organic frameworks,[23,24] and clusters.[25–28] However, the requirements for packaging, cost, safety, and performance have not been all attained.

Since it was experimentally synthesized in 2004,[29] graphene, which is a one-atom-thick layer of an sp^2-hybridized 2D allotrope of carbon, is versatile because of its large surface area,[30] mechanical properties,[31] light mass, and electronic properties.[32] Also, single-layer graphene has been successfully produced or synthesized in a variety of ways.[33,34] Nevertheless, graphene interacts with H_2 via weak physisorption, and thus, it is unlikely to achieve high adsorption capacity under realistic conditions that are required for large-scale applications. Previous theoretical and experimental studies show that graphene decorated with transition metals has high-capacity and reversible hydrogen storage.[35–37] Additionally, transition metals are connected with host materials and hydrogen molecules via Dewar[38] and Kubas[39] forces, respectively. These forces are generated via molecular polarization and hybridization between transition metal d orbitals and the H_2 σ^* orbital. Nonetheless, the carbon materials decorated with transition metals can suffer from metal oxidation and metal clustering caused by strong d–d orbital interactions, and these factors degrade the capacity.[40–43] Carbon-based materials decorated with alkali[44–46] and alkali-earth[47] metals that are uniformly and stably dispersed on the surface maintain high H_2 uptake, as indicated by related research. Lithium-doped graphene has been reported to be a potential

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vehicle for hydrogen storage because of its high gravimetric capacity of 12.8 wt%.[48] Chandrakumar *et al.* conducted an *ab initio* study and showed that fullerene functionalized with Li atoms (Na_8C_{60}) achieved a hydrogen adsorption density of ~9.5 wt% with six H_2 absorbed per Na atom.[49] Also, the relatively light weight of alkali metals enable it to be distributed in a discrete way for favorable gravimetric density of hydrogen. Agglomeration occurs when the cohesive energy between bulk metals is larger than their binding energy to adsorbents, and this drastically limits the efficiency of H_2 uptake.[41] Hence, the clustering bottleneck must be overcome to achieve a stable procession of hydrogen adsorption and desorption. Recently, a new type of graphene-like nanoribbons was successfully synthesized by Liu *et al.*[50] and Rong *et al.*[51] The nanoribbons are identified as net-Y and are a fascinating 2D carbon allotrope that consists of four-, six-, and eight-membered rings. Net-Y is energetically metastable, dynamic, and thermally stability, and net-Y is fabricated via the self-assembly of graphene-like nanoribbons.

On the basis of the above findings, in this contribution, Na-decorated net-Y was studied using a combination of density functional theory (DFT) and grand canonical Monte Carlo (GCMC) simulations to determine if it is capable of reversible and high-capacity hydrogen storage under moderate conditions. We are intrigued with net-Y as a proposed candidate for H_2 storage.

2. Calculation methods

Related calculations are implemented on the basis of DFT using the Vienna *ab initio* simulation package (VASP) with a projector augmented wave (PAW) method.[52,53] The Perdew–Burke–Ernzerh[54] formulation within the generalized gradient approximation (GGA) is chosen as the exchange correlation functional. Brillouin-zone integrations are performed according to the Monkhorst–Pack[55] scheme with $7 \times 7 \times 1$ k-points. A cut-off kinetic energy of 450 eV is set to expand the plane-wave basis. Geometrical optimization is fully relaxed until the forces acting on atoms are less than 0.01 eV/Å, the total energy is less than 10^{-5} eV, and a conjugate-gradient algorithm is used for ion-relaxation movement. We employed Grimme's DFT method to represent van der Waals interactions between the Na/H_2 molecule and the net-Y material. Further, GCMC simulations based on GDY are used to determine the hydrogen storage capacity under specific temperatures and pressures with 10^6 equilibration steps and 10^6 production steps. The 1s, 2p2s, and 3s electrons for H, C, and Na are treated as valence electrons, respectively.

3. Results and discussions

The optimized 2×2 supercell including 40 C atoms is shown in Fig. 1(a), in which the unit cell is also marked. Every C atom has three neighboring C atoms, which are labeled as a, b, and c with different colors and represent inequivalent adsorption sites. The optimized lattice parameters for the unit cell of net-Y are $a = 6.27$ Å, $b = 4.40$ Å, and $c = 20$ Å. To determine the most stable site for the Na atom, structure optimizations are first performed with pristine net-Y decorated with a single Na atom at thirteen possible adsorption positions, as illustrated in Fig. 1(b). Sites 1, 2, 3, and 4 are above the center of the C rings. Sites 5, 6, 7, 8, 9, and 10 are on the upper of bridge sites. Sites 11, 12, and 13 are on the top of the C atoms. We find that when the Na atom is situated at sites 5, 7, 9, 10, 11, and 13, it tends to transfer to site 3, whereas when the Na atom is at sites 8 and 12, it will move to site 4. When the Na atom is located at site 6, it prefers to occupy site 1 after optimization. Thus, it is initially judged that Na atoms can be absorbed to sites 1, 2, 3, and 4 steadily. Next, the adsorption energy (E_{ads}) of Na atoms to net-Y is calculated using the following formula: $E_{ads} = (E_{net\text{-}Y} + nE_{Na} - E_{Na/net\text{-}Y})$, where $E_{Na/net\text{-}Y}$, $E_{net\text{-}Y}$, and nE_{Na} are the total energies of the Na-decorated net-Y complex, pristine net-Y, and Na atoms, respectively. With one Na atom adsorbed, the adsorption energies for sites 1, 2, 3, and 4 are 1.96 eV, 1.61 eV, 1.80 eV, and 1.77 eV, respectively. This indicates that site 1 is most energetically favorable. Because of the structure's high symmetry, other seven Na atoms are added to the surface of net-Y on both sides, as shown in Figs. 1(c) and 1(d). The average binding energy of Na on the net-Y sheet is then evaluated using the equation mentioned above. The calculated average binding energy of Na to net-Y is 1.54 eV/Na, which exceeds that from pristine single-layer graphene[56] at the same amount of Na coverage. Meanwhile, the binding energy per Na is larger than the cohesive energy of bulk Na (1.13 eV), and this means that aggregation of Na atoms on pure carbon materials is suppressed. Also, the perpendicular distance between the Na atom above the center of the octagonal carbon rings and the net-Y layer is 2.04 Å. Also, the distance between neighboring Na atoms is 4.40 Å longer than that in the bulk Na crystal. In brief, eight Na atoms are uniformly and stably dispersed on both sides of net-Y.

To our knowledge, the structure of net-Y has been predicted using theoretical calculations, but it has not been synthesized experimentally to date. The main purpose of theoretically calculating hydrogen adsorption is to provide a possible reference for experiments. A stable structure is the precondition for hydrogen storage. Thus, we run first-principles molecular dynamics to examine the thermal stability of structures and to predict the possibility of experimental synthesis, and the results are shown in Fig. 2. The Nosé algorithm is used to control the temperature ranged to be around 300 K with total MD time of 8 ps with a time step of 1 fs. As seen in Fig. 2(a), the temperature varies wildly with an increase in time, whereas as seen in Fig. 2(b), total energy remains

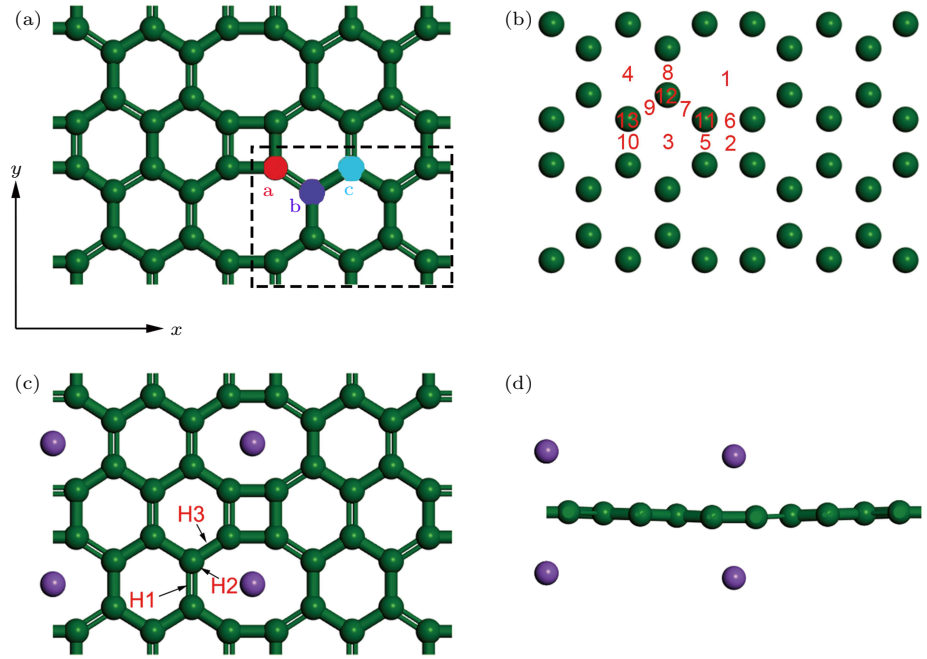


Fig. 1. (a) Scheme of the 2×2 supercell of net-Y with a unit cell indicated by the dashed lines. (b) Thirteen possible adsorption sites of Na atom are indicated by the numbers 1–13. Green balls represent carbon atoms. (c) Top view with three possible adsorption sites for the first H_2 molecule and (d) side view for optimized Na-decorated net-Y structure.

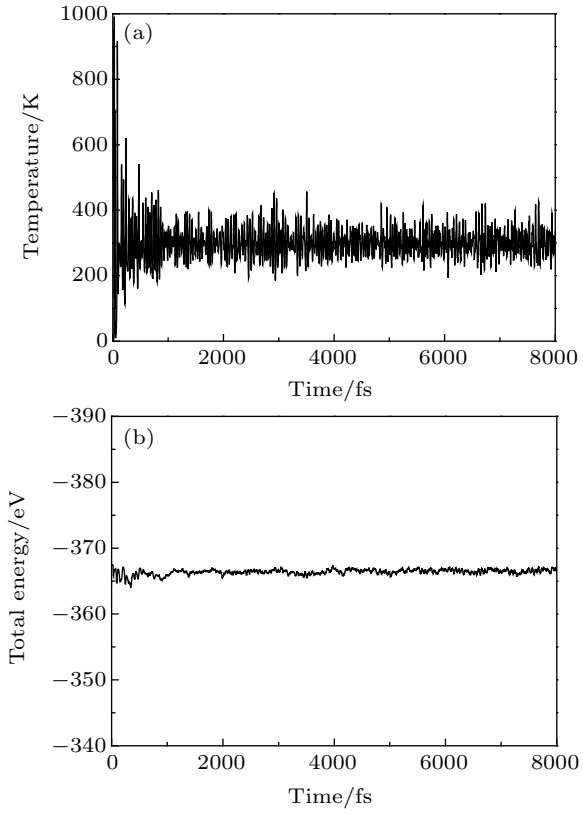


Fig. 2. Fluctuations in (a) temperature and (b) total energy for Na-decorated net-Y, each as a function of simulation time in first-principles MD simulations at 300 K.

nearly constant. These observations confirm the thermodynamic stability of Na-decorated net-Y under realistic work and experimental conditions.

We then turn to studying H_2 adsorption characteristics and storage capacity of Na-decorated net-Y. For adsorption of the first H_2 molecule, three initial positions are considered, as shown in Fig. 1(c) according to the symmetry of the structure. H_2 molecules are introduced into the Na-decorated net-Y layer, and we find that the first molecule prefers to occupy the H1 site, as shown in Fig. 3(a). Furthermore, it is very interesting from Fig. 3(b) that the second H_2 molecule is shared by two adjacent Na atoms. Moreover, more H_2 molecules are added to Na-decorated net-Y structures according to a symmetric distribution of H_2 molecules to investigate hydrogen absorption abilities; the geometries are fully optimized at each step, and the results are shown in Figs. 3(c)–3(d). A maximum of four H_2 molecules can be adsorbed for each Na atom, and the fourth H_2 molecule is parallel to the host material. The average adsorption energies of H_2 on the Na-coated net-Y complex are defined as $E_{\rm ad} = (E_{\rm Na/net\text{-}Y} + nE_{\rm H_2} - E_{\rm H_2/Na/net\text{-}Y})/n$, where $E_{\rm Na/net\text{-}Y}$, $E_{\rm H_2/Na/net\text{-}Y}$, and $nE_{\rm H_2}$ are the total energies of the Na-coated net-Y, H_2-adsorbed-Na-coated net-Y, and adsorbed H_2 molecules, respectively. After calculating, $E_{\rm ad}$ values for H_2 absorbed at sites 1, 2, 3, and 4 of Na-decorated net-Y are 0.25 eV, 0.32 eV, 0.30 eV, and 0.28 eV, respectively, and these values are within the range of favorable H_2 recycling for practical applications, which is 0.2–0.4 eV. All of the adsorbed hydrogen molecules surround a Na atom at distances of 2.30–2.50 Å, and these distances are shorter than that between Na atoms lying on pristine graphene.[57] Specifically, by comparison, we find that the second H_2 that is adsorbed has the longest H–H bond length, and this demonstrates that there is a strong interaction between the second H_2 and the two adjacent Na atoms.[58] This is consistent with the second adsorbed H2 molecule having the largest adsorption energy. Additionally, when each Na atom absorbs four H_2 molecules, the smallest H–H bond length is 0.76 Å, which is still longer than that of a

free H_2 molecule (0.74 Å).

To acquire further insights into the mechanism of H_2 adsorption, charge density differences of H_2 molecule absorption on Na-decorated net-Y are shown in Fig. 4. For H_2 molecules, electron accumulation forms close to Na, whereas electron depletion forms on the other side. This is an indication of the polarization of H_2, which leads to electrostatic forces between H_2 molecules and Na-coated net-Y. Adsorption of H_2 molecules on two adjacent Na atoms is seen in Figs. 4(b)–4(d). In particular, as marked by the red circle in Fig. 4(b), the most pronounced charge symmetrically accumulates between H_2 and two Na atoms, and this implies that the electrostatic interaction is strong and confirms that the largest E_{ad} is for the structure with two H_2 molecules adsorbed. Because of limited room, each Na atom can theoretically accommodate up to 4 H_2. This reaches a gravimetric capacity of 8.85 wt% hydrogen, which meets the 2020 U.S. DOE target.

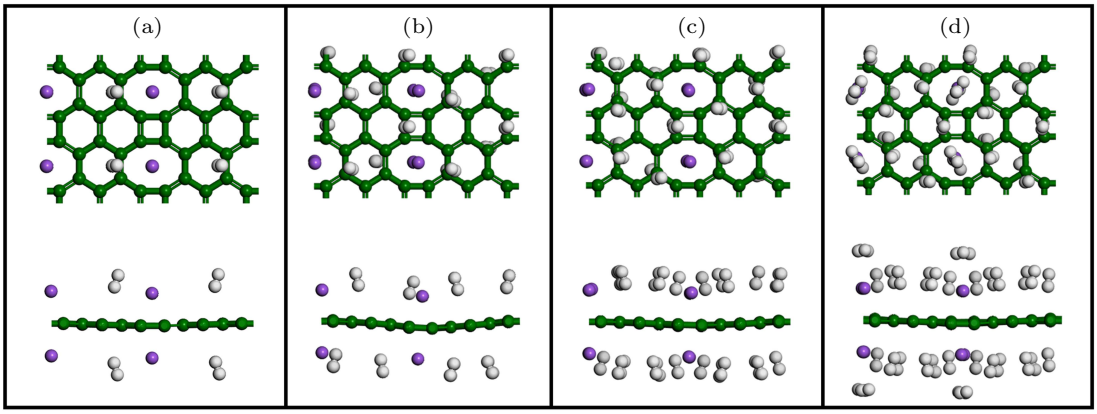


Fig. 3. Top and side views of optimized structures with (a) 1 H_2, (b) 2 H_2, (c) 3 H_2, and (d) 4 H_2 molecules absorbed. Purple ball is for Na, white ball is for H and green ball is for C.

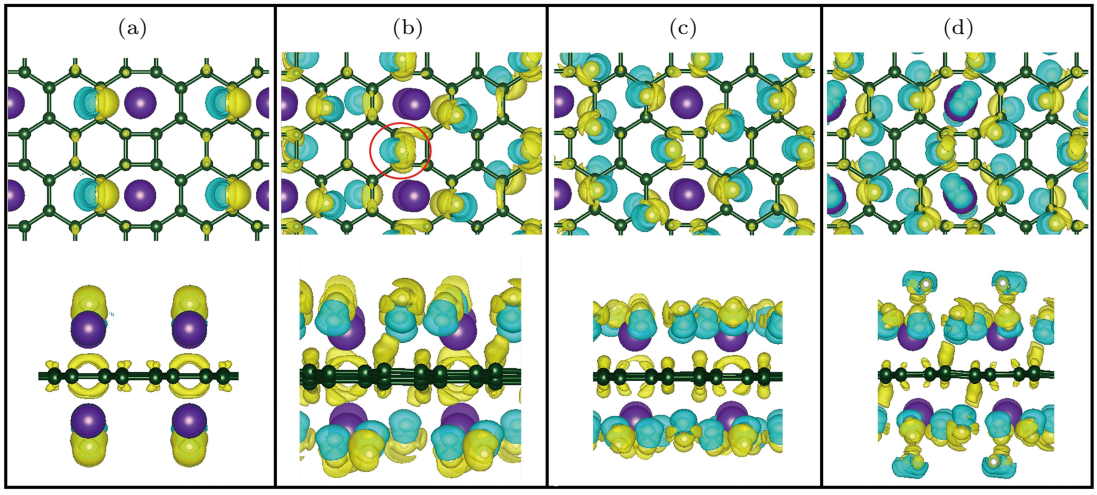


Fig. 4. Top and side views of charge density differences for H_2 adsorption on Na-decorated net-Y: (a) 1 H_2, (b) 2 H_2, (c) 3 H_2, and (d) 4 H_2. Light blue and yellow areas represent electron accumulation and depletion, respectively.

We perform the GCMC simulation to estimate gravimetric H_2 uptake based on a Dreiding force field[59] using classical molecular kinetic adsorption. The force field is used to describe the interaction between H_2 molecules and Na-decorated net-Y. The force parameters can be obtained by fitting the Morse equation:

$$U(r_{ij}) = D\left\{\exp\left[\alpha\left(1-\frac{r_{ij}}{r_0}\right)\right] - 2\exp\left[\frac{\alpha}{2}\left(1-\frac{r_{ij}}{r_0}\right)\right]\right\},$$

where r_{ij}, D, α, and r_0 represent the interaction distance, well depth, force constant, and equilibrium bond distance, respectively. The dependence of H_2 uptake gravimetric with pressure increasing at 233 K and 298 K are calculated from the GCMC simulations, and the results are shown in Fig. 5. An increasing monotonic trend of gravimetric density for H_2 is observed with an increase in pressure from 1 bar to 100 bar at both 233 K and 298 K. The expected gravimetric H_2 capacities of Na-decorated net-Y at 233 K are always larger than those at 298 K. Meanwhile, we note that H_2 gravimetric uptake can reach the 2020 U.S. DOE target at a low operating pressure of 30 bar at 298 K and 15 bar at 233 K. At 100 bar, gravimetric H_2 uptake of Na-decorated net-Y can reach 17.4 wt% at 233 K and 12.4 wt% at 298 K. Thus, the above results suggest that this material provides promising deliverable capacities.

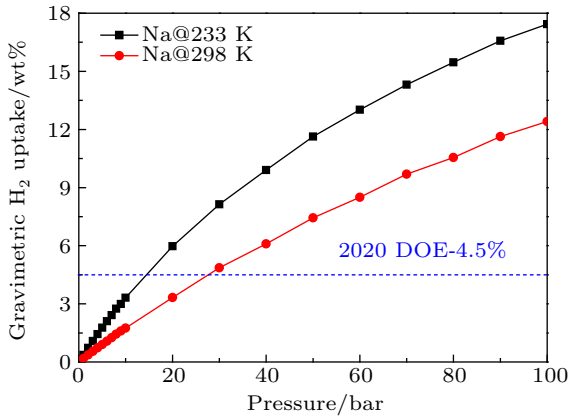


Fig. 5. Gravimetric hydrogen adsorption isotherms at 233 K and 298 K and for a pressure range up to 100 bars.

4. Conclusion and perspectives

In summary, we have used DFT calculations and tested the structural stability and hydrogen storage capacity of Na-decorated net-Y. It is demonstrated that a gravimetric density of 8.85 wt% with each Na atom surrounded by four H_2 molecules is obtained. Also, an interesting adsorption mechanism for the second adsorbed H_2 molecule, which is shared by two adjacent Na atoms, is found. GCMC simulations further verify that the net-Y carbon-based material is a prospective medium for hydrogen storage.

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