

Initial interactions between water molecules and Ti-adsorbed carbon nanotubes

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Spin-polarized first-principles calculations were employed to study the initial stages of water interactions with Ti-doped carbon nanotubes (CNTs), aiming to explore their potentials for water splitting to generate hydrogen or as practical hydrogen storage systems involving moisture. The rate-limiting barrier for splitting the first H₂O is 0.48 eV on a semiconducting (8,0) CNT, and 0.41 eV on a metallic (5,5) CNT. The barrier for splitting the second H₂O is only 0.12 eV, accompanied by the formation and release of a H₂ molecule. © 2007 American Institute of Physics. [DOI: 10.1063/1.2793182]

CO₂-exacerbated climate change and rapid depletion of fossil fuels have led to a global drive for clean energy resources. A promising solution is to use hydrogen as an energy carrier, particularly if it is produced with low CO₂ emission. However, current industrial methods of producing H₂ are via reforming hydrocarbons or refining petroleum: both still release CO₂ and neither is renewable.¹ Direct splitting of water holds great promise to generate H₂ without CO₂ emission. However, due to the exceptionally large kinetic barrier of a few eVs,² thermal splitting of water is only viable above 2500 °C.¹ Likewise, electrolysis of water also demands high energy with low yields and involves expensive catalysts.¹

Carbon-based nanomaterials have also been explored for hydrogen storage.^{3,4} While the hydrogen capacity of pure CNTs are under active debate,^{5,6} more recent studies of metal-catalyzed C nanostructures predict that up to four H₂ molecules can bind onto a Ti-atom adsorbed CNT, leading to a H₂ capacity of 8 mass %.⁷ Furthermore, fullerenes adsorbed with transition or light metals exhibit substantially improved H₂ capacities.⁸ Besides storage, an intriguing example is the theoretical demonstration that a graphene sheet with vacancies is able to provide multiple water dissociation pathways for H₂ production.⁹ In addition, a recent experimental study shows that highly ordered TiO₂ nanotube arrays can be used to photocleave water under ultraviolet irradiation.^{10,11}

Here we study the interactions of Ti-adsorbed CNTs with water molecules (1) to explore the possibility of hydrogen generation by water splitting and (2) to identify the effect of residual water in hydrogen on hydrogen storage. Several recent experimental¹² and theoretical^{13,14} studies have demonstrated the possibility of coating CNTs with Ti. Here we identify a remarkable catalytic effect on water splitting of the

Ti adatom on either a semiconducting zigzag (8,0) or a metallic armchair (5,5) nanotube as a nanosupport. When approaching a Ti-adsorbed (8,0) CNT, the first H₂O is readily split into an H⁺ and an OH⁻, each binding with the Ti adatom; the energy barrier is only 0.48 eV. This dissociation encounters a slightly lower barrier of 0.41 eV on a Ti-adsorbed (5,5) CNT. The splitting of the second water on the Ti adatom occurs with an even lower barrier of 0.12 eV. Furthermore, the two H atoms from the two split water molecules naturally combine to form a H₂ molecule, which is readily released. The processes identified here is important to the design of nanomaterials for hydrogen generation and storage.

The calculations were performed using the plane-wave based Vienna *ab initio* simulation package (VASP),¹⁵ implementing the generalized gradient approximation (GGA) for the exchange-correlation functional.¹⁶ A default plane-wave cutoff of 396 eV, from the GGA ultrasoft-pseudopotential database of carbon, was used.^{17,18} Ultrasoft pseudopotentials have been demonstrated to yield accurate electronic structures for first-row elements and localized *d* orbitals of transition metals with a relatively small energy cutoff for plane waves.¹⁷ To achieve the precision of the binding energy, three *k* points along the axis of the nanotubes were used for reciprocal space sampling, based on the Monkhorst-Pack scheme.¹⁹ All atoms were fully relaxed until the forces on any atom was <0.02 eV/Å. The (8,0) and (5,5) CNTs have diameters of 6.53 and 6.96 Å, respectively. To avoid potential influence of adjacent carbon nanotubes we constructed tetragonal supercells of 20.7 Å × 20.7 Å × 2*c* for the (8,0) CNT and 20 Å × 20 Å × 4*c* for the (5,5) CNT, where the axial lattice constants *c*=4.23 and 2.46 Å for the two CNTs, respectively. The “climbing image nudged elastic band” method²⁰ was applied to locate the transition-state geometries for the calculation of energy barriers.

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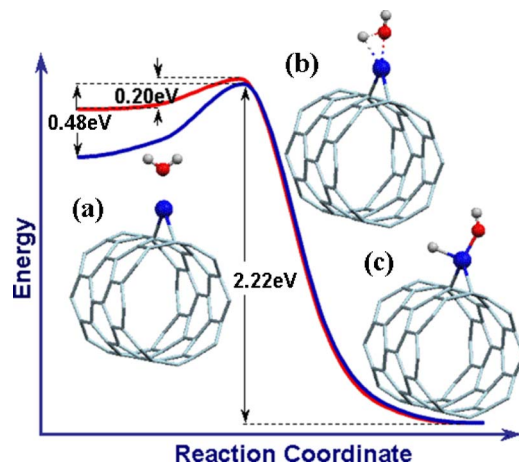


FIG. 1. (Color online) Optimized atomic structures and energy variations along the splitting pathway of the first H_2O on a Ti-adsorbed (8,0) carbon nanotube: (a) the initial, (b) the transition, and (c) the final states. The blue and red curves are from spin-polarized and unpolarized calculations, respectively. In Figs. 1–3, the blue, red, and gray balls denote the Ti, O, and H atoms, respectively.

When a single H_2O approaches the Ti adatom on the (8,0) CNT, the most stable binding structure before dissociation shows that the O atom is adsorbed on top of the Ti with an O–Ti distance of 2.15 Å [Fig. 1(a)]. The four atoms (Ti, O, H, and H) are nearly in the same plane through the center diagonal of a hexagon of the CNT. The binding energies from spin-polarized and unpolarized calculations are 1.04 and 0.72 eV, respectively, with a net magnetic moment of $2.52\mu_B$ for the former. In the final state [Fig. 1(c)], the H_2O has split into a H^+ and an OH^- , bound to the Ti adatom with an H–Ti bond of 1.73 Å and an O–Ti bond of 1.80 Å. The total energy of the system is the same from either spin-polarized or unpolarized calculation, lowered by 1.75 eV from the spin-polarized initial state.

The reaction barriers from spin-polarized (blue) and spin-unpolarized (red) calculations [Fig. 1] are 0.48 eV and 0.20 eV, respectively, which are significantly lower than that for water splitting in free space (~ 5 eV) or in liquid water (~ 1 eV).^{2,9} We note that the atomic geometry of the combined (CNT+Ti+ H_2O) system is essentially identical from both types of calculations, but the spin-polarized calculations always yield lower or equal total energies. In the transition state [Fig. 1(b)], one H atom detaches from the O atom to reach a H–O distance of 1.19 Å, while the other H atom maintains its bonding with the O atom.

To illustrate the binding between the H_2O and the Ti-adsorbed CNT, we plot the electron density difference in Figs. 2(a)–2(c) and the local density of states (LDOS) of H_2O and Ti in Figs. 2(d)–2(f) for the initial, transition, and final states, respectively. The electron density difference is derived by subtracting the electron density of H_2O and that of the Ti-adsorbed (8,0) CNT from the total electron density of the combined system. In the transition state, significant electron transfer from the d orbitals of Ti to the p orbitals of O has taken place [Fig. 2(b)]. The corresponding LDOS in Fig. 2(e) shows that the majority-spin d states of Ti near the Fermi level are largely depleted with respect to the initial state [Fig. 2(d)], which is consistent with the electron transfer in Fig. 2(a). In the final state, the main peaks below the Fermi level in the LDOS of H_2O characterize the bonding of H (at -2 eV) and OH (at -4 and -8 eV) with the Ti adatom

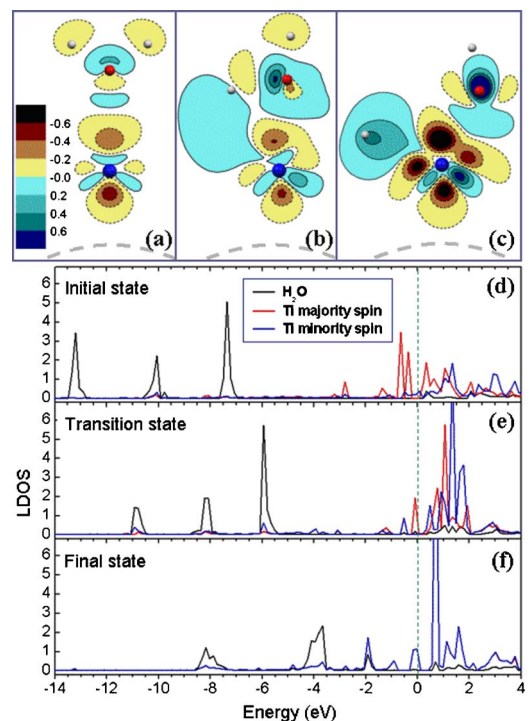


FIG. 2. (Color online) Electron density difference for (a) the initial, (b) the transition, and (c) the final states of the first water splitting on the Ti-adsorbed (8,0) CNT. The contour is drawn on a plane determined by Ti, O, and the H dissociated from the water molecule. The light gray dashed line outlines the position of the CNT. (d)–(f) are site-projected LDOS on H_2O and Ti for the initial, transition, and final states, respectively. The Fermi energy is denoted by the dashed (green) line.

[Fig. 2(f)].² Such information is instructive when spectroscopic techniques are applied to verify the splitting mechanism.

For the metallic nat (5,5) CNT, the adsorption energy of a Ti atom on the (5,5) CNT from spin-polarized calculation is 2.45 eV, comparable to that of 2.19 eV on the (8,0) CNT. The binding energy of an H_2O on the Ti-adsorbed (5,5) CNT is 1.17 and 3.19 eV for molecular and dissociative adsorptions, respectively. The energy barrier for the splitting process from spin-polarized calculation is 0.41 eV, lower than that of 0.48 eV on the Ti-adsorbed (8,0) CNT, as a result of a smaller charge transfer, by $\sim 0.1e$, from the Ti adatom to the metallic (5,5) CNT than to the semiconducting (8,0) CNT.

For an H_2O on a Ti atom in free space, the H_2O is split into an H^+ and an OH^- —both bind strongly to the Ti atom, with an energy barrier (from spin-polarized calculation) of 0.31 eV, lower than those on the (8,0) and (5,5) CNTs. However, it is impractical for a freestanding Ti atom to serve as an effective center for water splitting. Several experimental studies²¹ show that water is dissociatively adsorbed on Ti surfaces at room temperature, forming hydroxyl and oxide moieties. All the evidence indicates that CNTs are effective nanosupporters to preserve the strong catalytic property of Ti for water-splitting. Increasing Ti coverage should further reduce the energy barrier for such reactions, e.g., to 0.03 eV on a two Ti atom coadsorbed SWCNT from our calculations.

When a second H_2O is introduced to the Ti-adsorbed (8,0) CNT already hosting the first H_2O [Fig. 1(c)], both spin-polarized and unpolarized calculations yield the same nonmagnetic results for all the structures considered. Surprisingly, the energy barrier against the splitting of the sec-

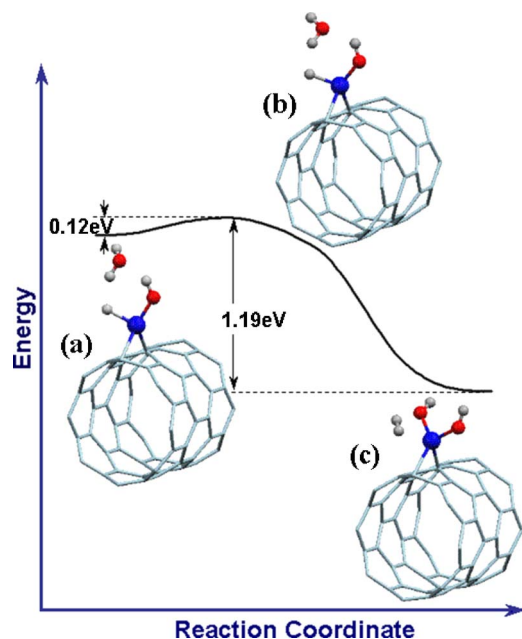


FIG. 3. (Color online) Optimized atomic structures and energy variation along the splitting pathway of the second H_2O on a Ti-adsorbed (8,0) CNT already hosting the first split water: (a) the initial, (b) the transition, and (c) the final states.

ond H_2O is only 0.12 eV, much lower than that encountered by the first H_2O (0.48 eV). Figure 3 shows the energy evolution along the reaction pathway and the corresponding structures of the initial, transition, and final states, respectively. Energetically, the dissociated water in the final state is still more stable than that in the initial state, by at least 1 eV. In particular, the two H atoms drawn from the two split water molecules naturally combine to form an H_2 molecule with an H–H distance of 0.76 Å. The adsorption energy of the H_2 is -0.13 eV, indicating that it can readily detach from the catalytic center, leaving an HO–Ti–OH complex on the CNT. Again, similar results are obtained for the Ti-adsorbed (5,5) CNT case.

It is also important to know the stability of the Ti atom on the CNTs as a catalytic center. The binding energy between the Ti atom and the (8,0) CNT changes slightly from 2.19 to 2.04 eV when the first water molecule is dissociatively adsorbed. When the second water is dissociated and the H_2 molecule released, the remaining HO–Ti–OH complex can still tightly bind on the (8,0) CNT, with a binding energy of 1.84 eV. For a uniformly Ti-coated (8,0) CNT, the average binding energy per Ti atom is as high as 4.3 eV.¹⁴ Hence, it is reasonable to assume that the Ti-coated CNTs are sufficiently stable to catalyze water splitting.

Bound with the OH^- , the Ti atom is likely to lose its catalytic activity. To sustain or restore its activity, the OH^- needs to be removed from the Ti atom, e.g., by photoexcitation or further reaction with other molecules. These intriguing

questions will be explored in future studies. The finding also indicates that Ti-doped CNTs can be effectively passivated by residual water when used for hydrogen storage.

Although the above DFT predicts binding energies and kinetic barriers at 0 K, thermal motions of ions at finite temperatures and zero-point motions of H only slightly modify the calculated energies, generally lowering the energy barrier by tens of meV.

In summary, we have investigated the kinetic steps in the initial stages of water splitting for potential hydrogen generation catalyzed by a Ti atom supported on either a semiconducting (8,0) or a metallic (5,5) CNT. We have shown that at least two water molecules can be dissociated consecutively by overcoming moderate energy barriers of only a few tenths of eV, accompanied by the formation and release of a H_2 molecule. The identified kinetic processes should be of fundamental importance to the eventual goal of low-temperature H_2 generation from water splitting and to the design of practical hydrogen storage systems.

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