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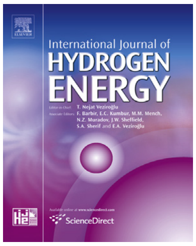

Yttrium dispersion on capped carbon nanotube: Promising materials for hydrogen storage applications

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ABSTRACT

Based on the density functional theory calculations, we predict that the Yttrium-dispersed capped-carbon nanotubes (CCNY) can serve as a high-capacity hydrogen storage material. The interaction of H_2 molecules with the CCNT can be significantly enhanced upon decoration by Y atoms. The H_2 molecules binding to the Y-CCNT system is similar to the Y–C_{60} system with a maximum of six H_2 molecules per Y atom and an average binding energy of −0.48 eV, which is suitable for reversible hydrogen storage at ambient conditions. With six Y atoms located, the gravimetric density of the cap is found to be 7.51 wt%, thus exceeding the 6.5 wt% target of the U.S. Department of Energy.

Introduction

Hydrogen energy is considered to be an ideal alternative to the existing fossil fuel due to its efficiency, abundance, and environmental friendly nature. The traditional methods of storing hydrogen as gas or liquid under high pressure can not achieve economical feasibility. Moreover, it brings security problems in practical applications. Therefore, the biggest challenge in hydrogen energy economy is finding materials which can store hydrogen with high gravimetric and volumetric density, and release the hydrogen molecules easily at ambient conditions.

Dillon et al. have pioneered the idea that single-walled carbon nanotube (SWCNT) can be the most promising medium for hydrogen storage owing to their stable structure, high surface-to-volume ratio and light weight density [1,2]. Later, Ye et al. and Liu et al. reported that SWCNT can store H_2 molecules up to 8.2 wt% and 4.2 wt%, respectively [3,4]. However, subsequent studies regarding this issue have come up with controversial conclusions that the hydrogen storage capacity of the pristine SWCNT is only 0.8 wt% at ambient conditions [5]. This is because the H_2 molecules are adsorbed to the surface of the SWCNT via van der Waals interactions with a binding energy of −0.1 eV/H_2, which is too weak for room temperature storage [6,7]. Recently, a lot of effort has been devoted to enhance the hydrogen storage capacity by doping alkali- and transition-metal atoms on the SWCNT [8–12]. Yildirim et al. demonstrated that a single Ti atom coated on the SWCNT can attach four H_2 molecules with three molecular and one dissociative adsorption [13].

Apart from the SWCNT, similar results were also reported for carbon- and boron-based nanomaterials (especially C_{60} and B_{80}) functionalized by alkali, light alkaline-

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earth and transition metals [14–19]. Our team have proposed that C_{60} decorated with 12 Yttrium atoms on each of its 12 pentagons is extremely stable and remarkably enhances the hydrogen adsorption capacity [20]. By DFT computations, Yoon et al. found that Ca is the most desirable coating metal element for functionalizing C_{60} fullerene with a hydrogen uptake of > 8.4 wt% [21]. Meanwhile, B_{80} buckyball coated with 12 Ca atoms on the pentagonal rings has been demonstrated to generate a gravimetric density of 8.2 wt% [22]. However, an immediate concern about these metal-doped nanostructures is the stability and possible cluster aggregation [23,24]. Besides, the number of H_2 molecules adsorbed at each site is still less, while the desorption temperature is quite high.

Capped-carbon nanotubes (CCNT) have received considerable attention due to their remarkable performance in field emission devices [25]. Depending on the diameter of the nanotubes, there are many different arrangements of pentagons and hexagons, which can attach the metal atoms separately and provide enough space to store H_2 molecules. Very recently we have predicted that metal-decorated CCNT can serve as a representative medium for hydrogen storage applications [26]. Chakraborty et al. have reported that Yttrium-coated SWCNT can serve as a potential hydrogen storage medium (6.1 wt%), and 100% desorption can be achieved in this system [27]. Inspired by their work, we show that a similar phenomenon occurs in Yttrium-dispersed CCNT. The hydrogen storage capacity of Y-decorated CCNT is greatly improved to 7.51 wt%, exceeding the United States Department of Energy (DOE) target of 6.5 wt% for hydrogen applications.

Method

The CCNT consists of a (5,5) SWCNT (50 carbon atoms) and a hemisphere of C_{60} (30 carbon atoms). In order to maintain electric neutrality, the dangling bonds at the end are saturated by hydrogen atoms [28,29]. All the geometry optimization and the energy calculations have been performed by the ab initio SIESTA code, in which improved Troullier–Martins pseudopotentials are used to describe the atomic cores [30,31]. Exchange-correlation effects have been treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) parameterization [32]. In our calculations, the plane wave cutoff is set at 200 Ry with the supercell size of $20 \times 20 \times 30$ $\mathring{A}^3$, which is large enough to prevent structures from their coupling. The Γ point is used to sample the Brillouin zone and all atomic positions are calculated by using the conjugate gradient method. The structures are fully optimized until the force on each atom is less than 0.03 eV/Å.

Results and discussion

We have carried out the calculations on CCNT structures containing a single Y atom located above the centers of both the pentagonal (P1 and P2) and hexagonal (H1 and H2) rings (Fig. 1). The binding energy of the Y atom is defined as

$$E_b(Y) = E(CCNT + Y) - E(CCNT) - E(Y)$$

and the negative binding energy indicates the system is stable. E(...) is the total energy of corresponding structure, and E(Y) is the energy of an isolated Y atom.

The binding energy of a single Y atom decorated on the hexagonal ring (−2.57 eV and −2.57 eV) is larger than that of the pentagonal ring (−1.98 eV and −2.08 eV), indicating that an isolated Y atom energetically prefers adsorption over a hexagonal ring. A similar phenomenon has arisen in Y-decorated C_{60} that the Y atom bound to a hexagon is more stable than that of a pentagon [20]. This difference can be attributed to the hexagon where the Y atom can interact with six carbon atoms, whereas in the case of pentagon the Y atom can interact with only five carbon atoms. The binding energy for Y atom on (8,0) nanotube is 2.20 eV [27]. Hence we expect that the Y atom will remain adsorbed on the CCNT during desorption of H_2 molecules. Additionally, our computational study reveals a shorter length of the Y–C bond for the Y atom adsorbed on H1 and H2 sites (2.49 Å and 2.51 Å) in comparison to adsorption on P1 and P2 sites (2.59 Å and 2.59 Å). It is consistent with the order of the overlap populations, which confirms that the interaction between the Y atom and the hexagonal ring is stronger than that of the other sites. It could be observed that there is an elongation in the C–C bond lengths under the metal dopant because of the loss of π-bonding interaction between the carbon atoms. We can see from Fig. 2 that, the Y atom has available empty d orbital, which results in their chemical activities as they are attached to the CCNT. After loading on the CCNT, the d orbital of isolated Y atom is broken and becomes partially occupied. At the same time, strong hybridization between the C-π and C-π^* orbital and the Y-d orbital can be observed as a result of the formation of the Y–C bond. According to the Mulliken method, we find a large amount of positive charges (~0.2 eV) accumulated on the Y atom, indicating that the Y atom is ionized and the electric field induced by the charge redistribution raises a possibility for hydrogen adsorption due to the polarization mechanism. This is also manifested by charge difference isosurfaces, as shown in Fig. 3. The charge difference isosurfaces are obtained by subtracting charge densities of Y atom and pure CCNT from that of CCNT+Y system, namely $\triangle\rho = \rho(CCNT + Y) - \rho(Y) - \rho(CCNT)$. It is clear that there is a significant charge accumulation between the Y-

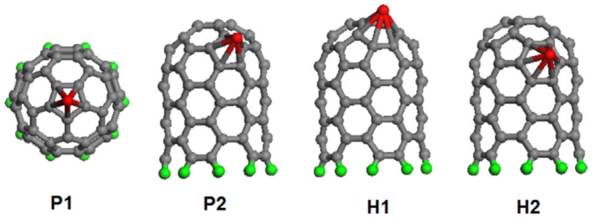

Fig. 1 – Optimized structures of the Y atom adsorbed at pentagonal (P1 and P2) and hexagonal (H1 and H2) hollow sites. The gray, red and green balls represent C, Y and H atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)