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Transition metal Ti coated porous fullerene $C_{24}B_{24}$: Potential material for hydrogen storage

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ARTICLE INFO

Article history:

Received 17 April 2015

Received in revised form

21 May 2015

Accepted 25 May 2015

Available online xxx

Keywords:

Fullerene

$C_{24}B_{24}$

Hydrogen storage

Density functional theory

ABSTRACT

The hydrogen storage capacity of transition metal Ti atoms decorated porous fullerene $C_{24}B_{24}$ is investigated by the pseudopotential density functional method. The $C_{24}B_{24}$ cage contains six B_4 rings with the average diameter of 3.88 Å. The Ti atoms are strongly bound to six B_4 rings. Each Ti atom can adsorb up to six H_2 molecules. The calculated average adsorption energies per H_2 for $(Ti-nH_2)_6C_{24}B_{24}$ ($n = 1-6$) are in the energy range from 0.24 to 0.55 eV, which is suitable for hydrogen storage at near-ambient conditions. The Dewar–Kubas interaction dominates the adsorption of H_2 on the outer surface of $Ti_6C_{24}B_{24}$. The largest hydrogen gravimetric density of $(Ti-6H_2)_6C_{24}B_{24}$ is 8.1 wt%, exceeding the 5.5 wt% by the year 2017 specified by the US department of energy (DOE). Therefore, the stable $Ti_6C_{24}B_{24}$ can be applied as one candidate for hydrogen storage materials at near-ambient conditions.

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Introduction

Because of the abundance, renewability, high efficiency, and environmentally friendly nature, hydrogen has been attracting much interest as an ideal kind of energy and has the potential to reduce our dependence on fossil fuels, helping to resolve the global warming issue [1]. However, it is a great challenge to find a material suitable for hydrogen storage. Recently, the U.S. Department of Energy (DOE) updated the hydrogen storage targets to a hydrogen gravimetric density of 5.5 wt% by the year 2017 [2]. The adsorption of H_2 through chemisorption is held by strong covalent bonds, and their dissociation requires high temperature. On the other hand, the adsorption of hydrogen molecules on materials via physisorption [3] is so weak that storage at near-ambient

conditions is not feasible. In general, materials that bind hydrogen molecularly with average adsorption energy per H_2 (E_{ad}) intermediate between physisorbed and chemisorbed states (0.2–0.6 eV) are good candidates to tailor the above requirements [4–6].

During the past decade, the hydrogen storage abilities of C-based nanomaterials like fullerene, carbon nanotubes, and graphene have been extensively studied. Due to the simple van der Waals interaction dominates the binding of hydrogen molecules to the surface of pure C-based nanomaterials, the surfaces cannot efficiently store hydrogen. However, their metal decorated counterparts such as $C_{48}B_{12}M_{12}$ ($M = Fe, Co, Ni$) [7], $M_{32}B_{80}$ ($M = Ca$ and Sc) [8], Rh coated carbon nanotubes [9], metal decorated graphene [10], Li_9C_{60} [11] have exhibited remarkable hydrogen adsorption capacity [12]. Unfortunately,

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<http://dx.doi.org/10.1016/j.ijhydene.2015.05.159>

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it is difficult to realize these metal decorated materials experimentally, since metal atoms tend to form clusters on the surfaces of nanostructures, and consequently the hydrogen storage capacity drops dramatically. Therefore, the binding energy of a metal atom to the substrate should be larger than the experimental cohesive energy of the bulk metal [13]. It was suggested that alkali metals (AM) and alkaline-earth metals (AEM) can produce a homogeneous coating due to their lightweight and low cohesive energies [8,12]. The hydrogen adsorption on these structures has been demonstrated experimentally, such as $\text{Li}_{12}\text{C}_{60}$ [13–15].

Experimentally, substitution the carbon atoms by the boron and nitrogen atoms in the C-based nanomaterials, such as fullerenes, carbon nanotubes, and graphenes, have already been realized [16]. Theoretically, the boron and nitrogen are the neighbors to carbon in the periodic table. It should be noticed that the N atom has one more valence electron than C, thus, the N doped nanomaterials are electron-rich complex and behave like donors, when the surfaces are decorated by the metal atoms, the electrons will transfer from the nanomaterials to the metal atoms, if these structures adsorb hydrogen, the metal atoms do not have enough hollow orbitals supplied to the electrons from the H_2 molecule, this obviously hinders the hydrogen storage ability. However, the boron atom has one less valence electron than C, so the B doped nanomaterials are electron-deficient, when the metal atoms decorate the surfaces, they will lose some electrons, therefore, the hydrogen molecules are strongly polarized by the charged metal positive ion, which is helpful for the adsorption of hydrogen [17]. This has been verified by the calculations on the hydrogen storage abilities of many metal decorated B-based nanostructures. For example, $\text{Sc}_{12}\text{C}_{48}\text{B}_{12}$ [18] has the better hydrogen storage capacity than that of $\text{Sc}_{12}\text{C}_{48}\text{N}_{12}$ [19]. $\text{Li}_{12}\text{C}_{48}\text{B}_{12}$ [20] exhibits more remarkable hydrogen storage ability than that of $\text{Li}_{12}\text{C}_{48}\text{N}_{12}$ [21]. Lu et al. [22] have found that the porous graphene by N doping obviously weakened the interaction energy between metal atoms and the porous graphene. On the other hand, the B atom is lighter than the N and C atoms, so the B doped hydrogen storage complex should have higher hydrogen gravimetric density than the N atom doped hydrogen storage structures. Therefore, the metal atoms decorated B-based nanomaterials should show the better hydrogen storage capacity and higher hydrogen gravimetric densities than the corresponding N-based nanostructures.

Recently, Guo et al. [23] have reported that the Ti atoms decorated untraditional fullerene cage Ti_6C_{48} could adsorb up to 36 hydrogen molecules. Later, Srinivasu et al. [24] have found that six transition metal atoms (Sc, Ti, V) decorated porous $\text{M}_6\text{C}_{24}\text{N}_{24}$ cages, particularly $\text{Ti}_6\text{C}_{24}\text{N}_{24}$, show remarkable hydrogen storage capacity at near-ambient conditions. More importantly, the transition metal atoms are bound to six N_4 rings in the $\text{C}_{24}\text{N}_{24}$ cage can effectively avoid the clustering problem. Inspired by this study, we choose the comparable more suitable transition metal atom Ti to decorate the B atom doped porous fullerene $\text{C}_{24}\text{B}_{24}$, and then use the density functional theory to study its hydrogen storage capacity. It is calculated that each B_4 ring in $\text{C}_{24}\text{B}_{24}$ has the average diameter of 3.88 Å and can be expected to effectively bind transition metal atoms, which can avoid the clustering problem. Each Ti

atom can adsorb up to six hydrogen molecules with the E_{ad} ranging from 0.24 to 0.55 eV, which are between physisorbed and chemisorbed states (0.2–0.6 eV). The hydrogen gravimetric density of the $(6\text{H}_2\text{--Ti})_6\text{C}_{24}\text{B}_{24}$ cage can reach 8.1 wt%, exceeding the 5.5 wt% by the year 2017 specified by US Department of Energy (DOE) [2]. Therefore, the $\text{Ti}_6\text{C}_{24}\text{B}_{24}$ cage can be applied as one candidate for hydrogen storage materials at near-ambient conditions.

Computational details

The calculations are performed with the generalized gradient approximation (GGA) [25] based on density functional theory (DFT) [26] as implied in the DMol³ package [27]. The Perdew–Burke–Ernzerhof (PBE) functional [28] and the double numerical basis sets including d-polarization functionals (DNP) are used. For all the hydrogen adsorbed structures, the Grimme method [29] for PBE/GGA is used for dispersion corrections. In addition, calculations are also conducted with another two exchange-correlation functionals, Wang and Perdew functional (PW91) [30] based on GGA and Perdew–Wang functional (PWC) [31] based on LDA, with the OBS method [32] considered for the dispersion interactions. The electronic structure is obtained by solving the spin-polarized Kohn–Sham [33] equations self-consistently. The DFT semi-core pseudopotential (DSPP) core-treat method [34] for the Ti atom and all-electron method for the C and B atoms are adopted. Self-consistent field procedures are done with a convergence criterion of 10^{-5} Hartree on the electron densities. The convergence tolerances are 2.0×10^{-5} Hartree, 0.004 Hartree, and 0.005 Å respectively for the energy, the max force, and the max displacement in the optimization. Finally, to obtain the electronic configurations of all the considered structures, the natural bonding orbital (NBO) electrons of all the structures are computed. The ground-state structures are determined by their minimal energies, which are further verified by no imaginary frequency in their harmonic frequency calculations.

The accuracy of our computational method is tested by computing the H_2 and the porous fullerene $\text{C}_{24}\text{N}_{24}$. The calculated bond length and binding energy (E_b) of H_2 are 0.75 Å and 4.55 eV, in good agreement with the experimental values of 0.74 Å and 4.53 eV respectively [35]. For $\text{C}_{24}\text{N}_{24}$, the calculated bond lengths of C–C and C–N are 1.55 Å and 1.34 Å, in good agreement with the results gotten by Srinivasu et al. [24] (1.56 Å and 1.34 Å) separately. Therefore, our computational scheme is suitable to study the structural and electronic properties of nanostructures.

Results and discussions

Fig. 1 schematically shows how to get the B-based fullerene cage $\text{C}_{24}\text{B}_{24}$ from C_{60} . As shown in Fig. 1, the generation course of B_4 rings are in the following: The two carbons indicated by the red ellipse in C_{60} and connecting two neighboring five-member rings are removed firstly, then, the four carbon atoms marked by the blue circle in C_{48} and connecting these two carbons are replaced by four boron atoms. It is known

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