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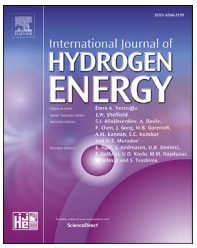

Transition metal atom Fe, Co, Ni decorated B_{38} fullerene: Potential material for hydrogen storage

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ABSTRACT

The hydrogen storage capacity of M-decorated (M = Fe, Co, Ni) B_{38} fullerene is investigated using first-principles calculations based on density functional theory. The Fe, Co, Ni atoms are strongly bound on hexagonal holes of B_{38} fullerene without clustering. Fe_4B_{38} (Co_4B_{38} and Ni_4B_{38}) adsorbs $24H_2$ with moderate average adsorption energy of 0.175 (0.184 and 0.202) eV/H_2. Based on density functional theory, the gravimetric density of Fe_4B_{38} (Co_4B_{38} and Ni_4B_{38}) could potentially reach 7.34 (7.21 and 7.22) wt%, respectively. Therefore, we infer that M-decorated (M = Fe, Co, Ni) B_{38} fullerene could be a candidate for further investigation as an alternative material for hydrogen storage.

Introduction

Hydrogen has been considered as an ideal energy due to its low cost, abundance and environmental friendly nature. Developments in the search for feasible hydrogen storage materials is one of the main challenges [1,2]. The U. S. Department of Energy (DOE) has promulgated the general standards: gravimetric hydrogen capacity of 5.5 wt% by the year 2017 [3]. The potential hydrogen storage capacities of metal decorated nanostructures have been identified recently based on density functional theory [4–9].

In fact, boron nanostructures are applicable for substrates because boron is lighter than carbon and can effectively bind with metal atoms. Metal decorated boron nanostructures have been widely analyzed for hydrogen storage using density functional theory [7,10–15]. However, Ca atoms cannot stably bind to B_{40} fullerene [10]. Based on density functional theory, the gravimetric hydrogen density of Na, K decorated B_{80} could potentially reach 11.2 and 9.8 wt% with average adsorption energies (E_{ad}) of 0.07 and 0.09 eV/H_2 [11]. Obviously, the average H_2 adsorption energy is too small to be applied at room temperature. Similarly, the average H_2 binding energy of the Li-C_{60} system is only 0.075 eV/H_2 [6]. Transition metal decorated carbon materials and boron materials show

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potential hydrogen storage properties. Shin et al. [9] find that Ni-dispersed C_{60} could be considered a novel hydrogen storage media potentially capable of storing 6.8 wt% with average adsorption energies of 0.33–0.42 eV/H_2. Tang et al. [16] report the potential hydrogen gravimetric density of Ti decorated $C_{24}B_{24}$ as 8.1 wt% with average adsorption energies of 0.24–0.55 eV/H_2. Based on density functional theory, Tang et al. [17] publish the largest hydrogen gravimetric density of Sc atoms decorated B_{40} fullerene as 8.3 wt% with average adsorption energies of 0.24–0.55 eV/H_2. Co, Ni decorated C_mH_m complexes could potentially store up to 3.49 wt% hydrogen with an average binding energy of about 1.3 eV based on density functional theory [18]. The fully decorated 4Ti@C_{28}@4Fe structure was found to retain up to 5.1 wt% of hydrogen at room temperature using density functional theory [19].

Most recently, Lv et al. has predicted the structure of B_{38} fullerene by using first-principles swarm structure searching calculations [20]. B_{38} is only a half size of B_{80}, and its mass is smaller than the half of B_{80} which could be conducive to improving the hydrogen storage properties. Using density functional theory, Lu et al. [21] analyzed the hydrogen storage of AM-B_{38} (AM = Li, Na, K, Mg, Ca). Among all of the complexes, Ca-decorated B_{38} appeared to be the best potential candidate for hydrogen storage with potentially high gravimetric density of 6.47 wt%. From their result, the average H_2 adsorption energy is so weak that it is not suitable for hydrogen storage at room temperature. We find using density functional theory, the potential gravimetric density of Ti-decorated B_{38} fullerene is 7.44 wt% with an average adsorption energy of 0.23 eV/H_2 [22]. To our knowledge, there has been no systematic theoretical reporting of the hydrogen storage of the transition metal atom decorated B_{38} fullerene (M = Fe, Co, and Ni). Thus, we will study the hydrogen storage capacity of M-decorated B_{38} by density functional theory (DFT) with GGA function. We will also investigate the stabilities and electronic properties of M-decorated B_{38}. When 4Fe (Co, Ni) atoms decorate on B_{38}, the potential maximum hydrogen gravimetric density is 7.34 (7.21 and 7.22) wt% with the average binding energy of 0.175 (0.184 and 0.202) eV/H_2.

Computational framework

All the density functional calculations were performed using the DMol^3 package [23]. We adopted the generalized gradient approximation (GGA) implemented in the exchange-correlation functional with the Perdewe Burkee Ernzerhof functional [24]. The van der Waals (vdW) interaction was described with dispersion-corrected DFT (DFT-D) [25–27] scheme, which is put forward by Ortmann, Bechstedt, and Schmidt (OBS) [28]. The double numerical polarized (DNP) basis was set in our calculations, and we used a double-DFT semi-core pseudo potentials (DSPP) treatment as the core treatment for relativistic effects. The self-consistent-field convergence tolerance was set to 1×10^{-6} Ha, the convergence criteria was 2×10^{-5} Hartree for energy, 5×10^{-3} Å for displacement, 4×10^{-3}Ha/Å for force. Spin unrestricted approach was applied, and smearing was set at 5×10^{-3} Ha. The global orbital cutoff of 5.5 Å was imposed in our calculations. We calculated the binding energy of transition metals on B_{38} fullerene using the following expression,

$$E_{ad}(M) = E(MB) - E(M) - E(B) \quad (1)$$

where E_{ad} (MB), E(M) and E(B) were the total energies of transition metal on B_{38}, an isolated metal atom and pure B_{38}, respectively.

The average adsorption energy of H_2 molecules on M-B_{38} complexes was determined by

$$E_{ad}[H_2] = [nH_2/E(MB) - E(MB) - nE(H_2)]/n, \quad (2)$$

where n was the number of H_2 molecules.

Results and discussion

M dispersion on B_{38}

B_{38} is highly symmetric and composed with hexagon and triangle holes. We first studied the structure of a single Fe (Co and Ni) atom on B_{38}. Fig. 1 shows the optimized structure of a Fe (Co and Ni) atom attached on B_{38}. "A, B, C" in Fig. 1 represent three kinds of adsorption sites for the Fe (Co and Ni) atom, "C" represents the B-B bridges around the hexagons and "A, B" are the centers of the two hexagons. "A" is the most stable position with the largest binding energy. The binding energy of Fe (Co and Ni) atom on B_{38} is 4.83, 5.52, 5.01 eV, which is larger than the cohesive energy of its bulk phases (4.35, 4.85 eV, 4.44 [29]). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap of B_{38} is 0.558 eV. The HOMO–LUMO gap of 1Fe-B38, 1Co-B38, 1Ni-B38 are 0.606 eV, 0.608 eV, 0.824 eV, respectively. The increase of the energy gap indicates that the systems have high dynamic stabilities.

Adsorption of H_2 molecules on Fe (Co and Ni) functionalized B_{38}

We first investigated one H_2 molecule adsorbed on the MB_{38} (M = Fe, Co, and Ni). Fig. 2(a–c) shows the most stable geometry configurations of $1H_2$-FeB_{38}, $1H_2$-CoB_{38} and $1H_2$-NiB_{38}.

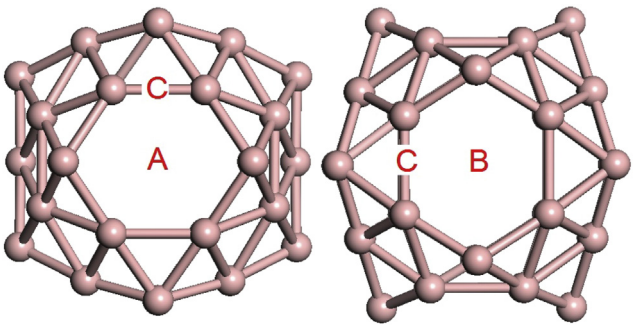

Fig. 1 – The optimized configuration of B_{38} fullerene. A, B and C represent the center of the two hexagon holes and the B–B bridge sites around the hexagon. Pink ball: B atom. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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