

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhydene

Ti-decorated zigzag graphene nanoribbons for hydrogen storage. A van der Waals-corrected density-functional study

A. Lebon ^{a,*}, J. Carrete ^b, L.J. Gallego ^c, A. Vega ^d

^a Laboratoire de Magnétisme de Bretagne, Université de Brest, F–29285 Brest, France

^b LITEN, CEA–Grenoble, 17 Rue des Martyrs, 38054 Grenoble Cedex 9, France

^c Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E–15782 Santiago de Compostela, Spain

^d Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, E–47011 Valladolid, Spain

ARTICLE INFO

Article history:

Received 23 September 2014

Received in revised form

11 December 2014

Accepted 30 December 2014

Available online 23 January 2015

Keywords:

Hydrogen storage

Graphene nanoribbons

H₂ saturation

ABSTRACT

We perform density functional calculations to investigate the adsorption of molecular hydrogen on Ti-doped zigzag graphene nanoribbons using a nonlocal van der Waals functional that has recently been proposed for accurate description of exchange and correlation effects in weakly bound systems. Our results show that the adsorption of a single H₂ molecule is dissociative in purely energetic terms, but there exists an energy barrier that prevents dissociation when the molecule is deposited on the Ti-doped graphene nanoribbon. When the Ti atom is adsorbed at a central or lateral hole site, each atom can bind up to four H₂ molecules, in each case satisfying the binding energy criterion specified by the U.S. Department of Energy for novel hydrogen-storage materials. On this basis, one can consider an effective hydrogen coverage on Ti-coated graphene nanoribbons with gravimetric density beyond the target of 6%.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen is a clean and abundant energy source that could perhaps replace fossil fuels in the future [1–5]. One of the main problems to achieve that goal is to find safe, cost-effective and practical means for storing hydrogen. Two of the main factors set by the U. S. Department of Energy (DOE) for novel hydrogen-storage materials are a good gravimetric density (the DOE target is ca. 6 wt%) and a binding energy of 0.2–0.6 eV per H₂ molecule [6,7], i.e. between the range of

physisorption and atomic chemisorption, which would allow storage and discharge to be cycled at ambient conditions.

Among the numerous materials that have been proposed as hydrogen-storage media, special attention has been devoted to carbon nanostructures, such as fullerenes, carbon nanotubes and graphene, because they are light-weight, inexpensive, and have large surface area, high thermal stability and exceptional mechanical properties (see, e.g., Ref. [8] and references cited therein). So far theoretical studies, generally performed using standard density-functional theory (DFT), have predicted that these materials could be used

* Corresponding author.

E-mail address: alexandre.lebon@univ-brest.fr (A. Lebon).

<http://dx.doi.org/10.1016/j.ijhydene.2014.12.134>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

as hydrogen storage media if they are doped or decorated with atoms of appropriate species, such as transition metals, aluminum, alkali metals and alkaline-earth metals. For instance, Yildirim and Ciraci [9] have used the generalized gradient approximation (GGA) [10] to show that Ti-decorated single-walled carbon nanotubes (SWCNTs) are potential high-capacity hydrogen-storage media. Extensive studies of the hydrogen uptake by light transition metals decorating various carbon nanostructures, such as linear carbon chains, graphene and SWCNTs, have been performed by Durgun et al. [11], Rojas and Leiva [12], Xiao et al. [13], López-Corral et al. [14], and Liu et al. [15] using also the GGA. The binding energies of early transition metals on GNRs are greater than the cohesive energies of the corresponding bulk metals, making them especially adequate to avoid metal clustering on such substrates, which could change the H₂ adsorption picture. Similarly, substitutionally Al-doped and Al-adsorbed graphene have been predicted to be candidates for H₂ storage on the basis of DFT calculations with the local-density approximation (LDA) [16,17]. Experimental studies on this kind of systems have also been carried out, although they are scarcer than theoretical studies due to the challenges that have to be overcome [18]. The pioneering work in this area was that of Dillon et al. [19], who investigated the storage of molecular hydrogen by assemblies of SWCNTs and porous activated carbon, obtaining a high enough hydrogen density as to meet the DOE requirement. More recently, Ghosh et al. [20] have investigated H₂ adsorption on graphene samples prepared by exfoliation of graphitic oxide and conversion of nano-diamond, obtaining H₂ uptakes of 1.7 and 3.1 wt% at (1 atm, 77 K) and (100 atm, 298 K), respectively. In contrast, recent experimental studies on SWCNTs-Ti metal composites have found an efficient hydrogen uptake of up to 4.74 wt%, showing 100% desorption in the temperature range of 433–583 K and a hydrogen average binding energy of 0.4 eV [21].

A carbon nanostructure that has attracted great attention of late is the graphene nanoribbon (GNR), an (unrolled) graphene strip of nanometer size. GNR-based systems have been shown to have many applications in nanoelectronics, spintronics, and optoelectronics (see, e.g., Refs. [22–24] and references cited therein), and their H₂ storage capacity has been investigated using standard DFT methods. For instance, Ca-decorated [25] and Sc-decorated [26] GNRs have been predicted to satisfy the binding-energy and gravimetric requirements specified by the DOE on the basis of the GGA. Recently, we have also used the GGA to investigate hydrogen-passivated zigzag GNRs bearing adsorbed Sc, Ti or V atoms, reaching the conclusion that, of the three systems investigated, Ti/GNR and V/GNR appear to satisfy the binding-energy criterion H₂-storage materials [27]. We note that although Ca-decorated graphene-based nanostructures have been proposed for H₂ storage on the basis of the low cohesive energy of bulk Ca (which apparently would prevent Ca clustering on that substrate), DFT studies performed by Nakada and Ishii [28] on the migration energy of Ca atoms on graphene gave a value as low as 0.07 eV for the diffusion barrier, which would enable the Ca atoms to move easily on the graphene layer. In contrast, the migration energy of the slightly heavier Ti atom (whose binding energy on graphene is greater than the

cohesive energy of the corresponding bulk metal) is one order of magnitude higher, 0.60 eV [28].

Recently, the accuracy of standard DFT methods for describing weakly interacting systems has been questioned due to their not accounting correctly for the ubiquitous van der Waals (vdW) forces [29,30]. These forces, which derive from quantum mechanical charge–fluctuation correlations, are accounted for by exact DFT, but the commonly used LDA and GGA employ only local and semi local densities, respectively, and thus cannot in principle describe non local, long-range vdW interactions. In recent years, several DFT methods have been proposed that do reflect vdW forces more or less closely (for a review, see Ref. [31]). One of the most rigorous and efficient methods was developed by Dion et al. [32], who obtained a non local vdW density functional that employs only the electron density as input. Modified forms have been recently proposed, which for some systems are even more accurate than their precursor [33,34].

In view of the above findings, the question arising is whether the conclusions about the affinity of carbon-based nanostructures for molecular hydrogen that have recently been inferred on the basis of standard DFT methods are modified when vdW-corrected DFT approaches are used. In this work, we analyze in detail this issue by considering the Ti/GNR nanostructures that we have recently investigated [27]. Apart from investigating if, under vdW-corrected DFT, Ti-adsorbed GNRs satisfy the DOE H₂-binding energy criterion, our work has two other main objectives. First, we wish to investigate if adsorption of a single H₂ molecule on Ti/GNR is molecular rather than dissociative, for which purpose we calculate the possible energy barrier between these two configurations. Second, we want to analyze if Ti/GNR systems fulfill the gravimetric target of ca. 6 wt% hydrogen; hence we calculate the maximum number of H₂ molecules attached to a single Ti atom adsorbed on the GNR, and subsequently estimate the hydrogen density coverage on a Ti-coated GNR. An interpretation on the characteristics of H₂ adsorption on the Ti/GNR system is performed by means of a careful analysis of the electronic structures. Details of the computational procedure used in this work are given in Sec. [Computational procedure](#), our results are discussed in Secs. [Structures and energetics](#), [Electronic features](#), and [Estimate of the hydrogen coverage on a Ti-coated GNR](#), and in Sec. [Conclusions](#) we summarize our main conclusions.

Computational procedure

Most of our simulations are run using the SIESTA package [35], which employs localized numerical atomic orbitals as basis sets in the solution of the single-particle Kohn–Sham equations. vdW-corrected DFT calculations are performed using the optB88-vdW functional proposed by Klimeš et al. [34], which optimizes predictions for a set of 22 weakly bonding dimers. The efficient application of these non local corrections in SIESTA is due to Román-Pérez and Soler [36]. We note that in a recent paper on H₂ adsorption on Al-doped GNRs we showed that the GGA yielded H₂ binding energies similar to those obtained using the optB88-vdW functional, although the GGA underestimated binding energies on pristine GNRs [37].

Download English Version:

<https://daneshyari.com/en/article/1271608>

Download Persian Version:

<https://daneshyari.com/article/1271608>

[Daneshyari.com](https://daneshyari.com)