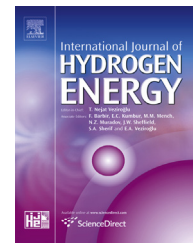




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Insights into the hydrogen dissociation mechanism on lithium edge-decorated carbon rings and graphene nanoribbon

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ABSTRACT

The purpose of this study is to show that H₂ is easily dissociated on lithium edge decorated carbon systems to form strong C–H and Li–H bonds. This mechanism has not been considered in previous studies where these kinds of systems have been proposed as good candidates to serve as hydrogen storage materials. The reactivity of molecular hydrogen (H₂) on three representative lithium edge-decorated carbon systems (on the clusters C₅Li⁺ (1) and C₆Li₆ (2), and on lithium edge-decorated zig-zag graphene nanoribbon (GNR-Li) (3)) have been studied using ab initio calculations based on the density functional theory with dispersion-corrected van der Waals exchange correlation functional. Our calculations show, on the one hand, that heterolytic hydrogen dissociation can precede with relatively low reaction barriers (0.60, 0.45 and 0.56 eV for systems 1, 2 and 3, respectively) along the minimum energy path and, on the other hand, that chemisorption energies are highly stabilizing (in the range of 1.15–1.54 eV). It is important to note that the highest activation barrier is found for the unique system, characterized as global minimum, on its corresponding potential energy surface (PES), which is system 1. These findings suggest that reversibility of the hydrogen absorption/desorption reactions, required in promising hydrogen storage materials, does not apply in these systems.

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Introduction

The development of reliable and environmentally friendly approaches for energy conversion and storage is one of the key challenges that our society is facing nowadays [1–5]. Fuel cell devices, in which electrical energy is generated by the conversion of chemical energy via redox reactions at the anode and cathode, have now become a major research area [6–10]. The chemical energy density of hydrogen is 142 MJ/kg, which is more than three times the one of gasoline and the by-product of its combustion is water. Thus, hydrogen is one of the most interesting “green” fuels. In this context, graphene and derived compounds, have been proposed as reliable materials that can help to address the two main issues related to the use of hydrogen as fuel: (i) production and (ii) storage/transportation [11–18].

Even though both issues are important, we will now turn our attention to the latter. Many theoretical investigations suggest that the adsorption capacity of hydrogen on graphene is increased by suitable metal doping modifications, thus making two kinds of molecular interactions possible. The first one is based on the polarization of H_2 by the electric field established by alkali, or earth alkali metals, leading to H_2 binding energies of approximately 0.2 eV [19–23]. The second one is based on the so-called Kubas interactions [24], where the transition metal orbitals are combined with the hydrogen orbitals to achieve binding energies between 0.2 and 0.6 eV. These stabilizing interactions make these materials potentially useful for hydrogen storage [25–29].

Motivated by this increasing need for suitable hydrogen storage materials, other researchers have focused on testing other carbon-based materials. For instance, Sun and co-workers proposed, *in silico*, the cluster $Li_{12}C_{60}$ (where each Li was individually placed in order to cap each of the twelve pentagons of the fullerene) as a potential hydrogen storage system [19]. The authors suggested that, due to the difference in electronegativity between Li and C, the Li atoms have a positive partial charge, favoring an ion-induced dipole electrostatic interaction with the H_2 molecule; which, in turn, induces the H_2 adsorption on this system.

More recently, two lithium edge decorated carbon aromatic clusters have been proposed as promising systems for hydrogen storage [30–33]: the hexalithium benzene (C_6Li_6) and the $C_5Li_7^+$ cluster [34]. It is important to note that the star-shape is the global minimum energy structure for $C_5Li_7^+$, for C_6Li_6 it is only a local minimum on the corresponding potential energy surface [35].

Quantum chemical calculations predicted that the first one can trap between 6 and 12 H_2 molecules (involving a non-dissociative H_2 interaction) with a good gravimetric weight percentage of adsorbed hydrogen (9.6 wt%) [30,32]. Whereas in the second one, each Li center can bind up to three H_2 molecules, which leads to a noticeable gravimetric weight percentage (28.0 wt%) [31]. However, this exceptional hydrogen storage capability is supported only on the non-dissociative H_2 adsorption on the cluster surface. Moreover, different to what happens in lithium doped graphene sheets, fullerenes and nanotubes (where lithium is bonded by electrostatic interactions involving lithium and the delocalized π -cloud of the

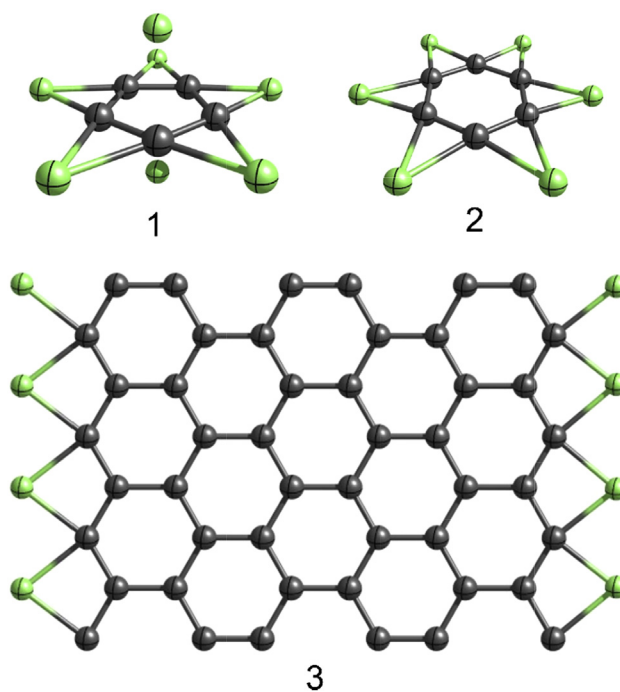
systems) [19,36], in lithium edge decorated carbon systems, it is expected that electrostatic interaction, between lithium and carbon, mainly involves the σ -cloud of the systems. This has important implications on the reactivity of H_2 on this class of materials.

In order to gain a better understanding of the H_2 interaction with any chemical system, it is mandatory to evaluate the viability of the H_2 dissociative adsorption. If the H_2 dissociation were an energetically favored process, it would have two key implications: on the one hand, the chemisorption would change drastically the H_2 release energies; and on the other hand, the cleavage and formation of new chemical bonds could transform the material irreversibly.

In this work we present a computational study to explore the energetic viability and the mechanism involved in a dissociative interaction of H_2 with three representative lithium edge-decorated carbon systems. The first two are the clusters $C_5Li_7^+$ (1) and C_6Li_6 (2) mentioned above. Whereas, system 3 consists of a lithium-decorated zig-zag graphene nanoribbon (GNR-Li), with periodicity along the zig-zag direction, as depicted in Scheme 1.

Computational methods

As a first approximation on the H_2 interaction with the C–Li clusters (systems 1 and 2), collisions between one H_2 molecule and these systems were performed. They were simulated using Born–Oppenheimer molecular dynamics (BO–MD) [37], with a time step of 1 fs and the total time of the dynamics was 5 ps. The temperature was fixed at 273 K and, in order to keep the total nuclear energy fixed, the velocities were rescaled at each step. These calculations were performed at the ω B97X-D



Scheme 1 – Equilibrium geometries of the three systems under study: $C_5Li_7^+$ (1), C_6Li_6 (2) and GNR-Li (3).

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