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Electronic properties and hydrogen storage application of designed porous nanotubes from a polyphenylene network

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ABSTRACT

Based on a polyphenylene network, a series of porous graphene nanotubes (PGNTs) are created and optimised via density functional theory calculations. The calculated band dispersion of the two-dimensional porous graphene can be tuned by rolling it into nanotube form. To explore the energy application of PGNTs, we studied H₂ adsorptions on metal (Li, Ca, and Na) decorated structures of PGNTs as well as B-substituted PGNTs. The results indicate that both the curvature effect and B substitution can strengthen the metal binding and prevent the metal atoms from clustering. Particularly for H₂ adsorption, modification of the electronic property by the curvature effect is beneficial to provide more accessible space, leading to much higher adsorption energies of H₂ on PGNTs than that on planar porous graphene, which is promising for the practical application of hydrogen storage.

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Introduction

Currently, some new energy resources are recommended as alternatives, such as hydrogen energy, solar energy, wind energy, nuclear energy, etc. [1,2]. Hydrogen gas (H₂), one of the most ideal energy carriers, has attracted extensive attention because it possesses many crucial advantages, including

environmental cleanliness, renewability, abundance, and high gravimetric energy density. In recent years, a considerable number of researchers have devoted themselves to exploring the utilisation of H₂ using a safe and economic method under realistic environmental conditions. Unfortunately, the H₂ storage capacities in current host materials are insufficient to realise commercialisation [3]. Towards achieving the “Hydrogen Economy”, it is necessary to enhance

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the capacities of H₂ storage of materials or to search/design new materials with high H₂ uptakes at ambient temperature and safe pressures.

As interesting candidates, porous materials (PMs) have been widely studied for H₂ storage in the past decade [4–8] because they have high surface areas and large void spaces for H₂ guesting. In addition, the mechanism of H₂ storage in PMs is primarily physical sorption, which, compared with the chemical sorption, has advantages of fast kinetics and complete reversibility without extreme conditions. Recently, many PMs have been proposed for use in gas storage, including metal organic frameworks (MOFs) [9–12], covalent organic frameworks [13–16], conjugated microporous polymers [17–19], porous carbon-based materials [20–23], and so on. Note that all of the above-mentioned PMs have a carbonaceous component, which greatly influences the H₂ storage capacities in PMs due to its high surface area [24]. Importantly, carbon materials (CMs), including fullerenes [25], carbon nanotubes [26], graphene [27,28] and graphyne [29,30], have been tested as H₂ carriers, and some investigations have demonstrated that CMs are promising as a H₂ storage medium when various modifications are performed [25–32]. Overall, functionalised CMs could play an important role in H₂ storage in future works.

Graphene [33], a famous two-dimensional (2D) CM, has increasingly become the focus of research due to its fantastic properties and potential applications in sustainable energy areas. Subsequently, graphene-related materials, even though non-carbon 2D materials, have become popular topics of scientific research in academia and in industry [34–40]. Porous graphene (PG), a 2D graphene-like material with periodic pore distribution, was successfully synthesised on metal surface via a coupling reaction of pre-designed molecular building blocks [41]. PG has been extensively studied due to its versatile applications, such as gas purification or separation [42–44] and H₂ storage [2,23]. Due to the large surface area, 2D materials have been proposed as one of the most promising candidates for H₂ adsorption. Nevertheless, it has been reported that the interaction between H₂ and the carbon framework is very weak, and the adsorption energy (AE) of H₂ on a PG surface is too low to satisfy the requirements of practical applications.

To improve the H₂ storage capacity of PG, the surface has been chemically modified through introducing heteroatoms, such as metal doping and boron/nitrogen substituting. Du et al. [2] studied the adsorption behaviour of an H₂ molecule in a Li-decorated PG using first-principles calculations based on the local density approximation, and they found that each Li atom can adsorb three H₂ molecules, with an average AE of approximately 0.25 eV on PG, resulting in a theoretical capacity of 12 wt%, which is much higher than the target of 5.5 wt% set by the U.S. DOE in 2011 [45]. Reunchan et al. [46] also theoretically studied the interaction between H₂ and metal-dispersed PG and demonstrated that Li, Na, and Ca atoms can be stably adsorbed on PG at the centre of six-carbon rings in the form of ionised-metal as a result of charge transfer from metal to PG, while multiple H₂ molecules can be further adsorbed around metal atoms, based on static multiple Coulombic interactions. Similarly, our previous work noted that the mechanism of H₂ adsorption on Li-MOFs is mainly

due to the charge transfer between Li and H₂ [11]. Recently, Huang et al. [47] found that Li-doped oxidised PG is highly attractive for use in H₂ storage.

The above-mentioned results are based on standard density functional theory (DFT), which is not adequate to describe the weak interaction between H₂ and host materials, and in practical utilisation, the H₂ uptake at approximately room temperature will be quite reduced compared to the simulated results. Moreover, pristine PG has small binding energies to metal atoms, much smaller than the cohesive energy of metals, which cannot completely prevent metal atoms from clustering. Therefore, we considered the influence of B substitution on metal doping and on the following H₂ adsorption using multiscale simulations. The results indicate that the B-substituted PG increased the AE of both Li and Ca, as well as that of H₂ [23]. Grand canonical ensemble Monte Carlo (GCMC) simulations indicate that B-substituted PG combined with Li/Ca doping exhibits a good performance of H₂ storage at room temperature, exceeding 6 wt% [23].

On the one hand, although the performance of PG material on H₂ storage has been claimed to be good, the storage capacity will decrease significantly when introduced in storage equipment used in practical application. Thus, we must continue to improve the H₂ storage capacity of PG. On the other hand, our work regarding graphyne [29] indicated that the numbers of hydrogen molecules from GCMC and *ab initio* molecular dynamics at room temperature and from dispersion-corrected DFT calculations are almost the same, which should be caused by the lack of spatial positioning for H₂ adsorption. We also noticed that pioneering studies regarding the H₂ uptake on metal-dispersed PG surface encounter this deficiency, that is, the distance between doped metal atoms is too short for them to fully play their role in H₂ adsorption. Consequently, we infer that lengthening this distance could be an effective way to enhance H₂ adsorption. Herein, we attempt to extend the distance between doped metals on PG through bending the 2D structures. To this end, we roll PG into nanotubes (denoted as PGNTs), as displayed in Scheme 1, and the name rule follows the transition of graphene into carbon nanotubes.

Many studies have explored hydrogen storage in various tubes [26,48–52], and interestingly, similar carbon nitride nanotubes have been produced and their structural and optical properties for selected chiralities were investigated [39]. Additionally, some applications including Li storage and hydrogen storage have been explored in graphitic carbon nitride nanotubes [40]. Motivated by the hydrogen adsorption investigations of nanotubes and PG materials, we will highlight the combination of pore-containing and tube-forming conformations for significant improvement of metal doping and hydrogen storage properties. To the best of our knowledge, no experimental evidence exists regarding hydrogen adsorption on the PGNTs, which have yet to be synthesised in experiments. The presented theoretical design will provide inspiration for future experimental endeavours to utilise PG (and other 2D materials) as a gas storage carrier. In this work, Li, Ca, and Na atoms are selected as doping atoms, from which we can explore the curvature effect on the distance of metal atoms as well as on H₂ adsorptions. Because B substitution has been proven to be a useful method to enhance metal binding

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