RESEARCH ARTICLE

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Computational Design of 3D Porous Aluminum Nitride Assembled From AlN-Biphenylene Nanoribbons for Reversible Hydrogen Storage

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Hydrogen fuel with zero CO_2 emission is of current interest for global carbon neutralization. In this study, a 3D porous aluminum nitride (*p*-AlN) framework assemble from AlN-biphenylene nanoribbons and investigate its performance in reversible hydrogen storage is presented. Using density functional theory (DFT), it is showed that the *p*-AlN is dynamically and thermally stable, and exhibiting a semiconductor nature with a bandgap of 3.57 eV. The adsorption energy of H_2 is in the range of −0.104 to −0.087 eV/H_2. According to ab initio molecular dynamics (AIMD) simulations, the H_2 molecules remain stable above liquid nitrogen temperature (77 K). The studied system offers gravimetric (volumetric) capacities of 4.95 wt.% (67.86 g L^{-1}) at 77 K/35 bar, and 1.41 wt.% (18.71 g L^{-1}) at 298 K/100 bar, as revealed by grand canonical Monte Carlo (GCMC) simulations based on force field parameters fitted from DFT results.

1. Introduction

The transition from fossil fuels to sustainable energy sources is essential for reducing global CO_2 emissions and mitigating climate change. Hydrogen, recognized for its high energy density and zero carbon emissions, is a key candidate as an energy carrier for future clean energy systems.[1] However, the low gravimetric and volumetric energy densities along with the sluggish kinetic diffusion of H_2 are the major hurdles in developing efficient and safe hydrogen storage systems.[2] Conventional storage methods, such as compressed gas under high pressures (>350 bar) or cryogenic liquid storage at 20 K, are limited by low energy density, high costs, and safety concerns, prompting the need for advanced storage materials that can safely and effectively store hydrogen at practical temperatures and pressures.[3,4] The U.S. Department of Energy (DOE) has set targets of 5.5 wt.% gravimetric and 40 g L^{-1} volumetric capacities for hydrogen storage systems by 2025.[4]

In this regard, storage of hydrogen in solid state materials offers a promising solution. For example, solid porous materials of current interest[5] such as zeolites,[6] metal-organic frameworks (MOFs),[7] and carbon-based structures[8] are efficient in hydrogen storage due to their tunable properties and large surface areas. However, their performance is often limited by weak physisorption interactions resulting from the low polarizability of H_2 molecules.[9] To enhance H_2 interaction, researchers have explored doping these materials with alkali, alkaline earth, or transition metals (TMs), which improve their chemical activity and create more active sites that strengthen hydrogen adsorption. Doping with TMs can improve the absorption, but the large mass of TM atoms can reduce the gravimetric density. Furthermore, doping can lead to the clustering of TM atoms.[10] Therefore, current techniques for improving the interaction between H_2 and porous materials focus on designing porous materials with intrinsic open metal sites. A recent study discovered that porous TiC_2 has a hydrogen adsorption energy of −0.355 eV/H_2, resulting in a storage capacity of 4.0 wt.% and 106.0 g L^{-1} at 16 bar/230 K. Such a high performance is attributed to the Kubas interaction mechanism.[11] Additionally, NU-2100 ($C_6H_3Cu_2N_6$) recorded adsorption energy of 0.331 eV and a storage capability of 10.4 g L^{-1} at 100 bar/233 K.[12] These findings highlight the potential use of new porous materials with intrinsic open metal sites for hydrogen storage.

Among the studied systems, aluminum (Al^{3+}) -based materials are of special interest.[13–15] Al is known for being lightweight, inexpensive, and abundant, making it an attractive option in hydrogen storage applications. Wang et al. have explored the potential in the AlN-based nanostructures in various forms, including nanocages, nanocones, nanotubes, and nanowires. In these structures, the Al site can bind one hydrogen molecule through charge polarization with an adsorption energy of −0.2 eV/H_2 and a capacity of 4.7 wt.%.[16] In nanoporous materials, for example, $Al(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$, the storage capacity can reach to 3.8 wt.% at 1.6 MPa/77 K.[17] Additionally, Evans et al. experimentally studied aluminum formate ($Al(HCOO)_3$), known as ALF, which offers adsorption energy of 0.089 eV, and can uptake 12 g H_2/kg of the ALF at 25 bar/120 K.[18] Moreover, the ultraporous MOF NU-1501-Al, designed using simulation-motivated synthesis,

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