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Designs of fullerene-based frameworks for hydrogen storage

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Two types of hybrid metallofullerene framework are theoretically designed, and their structural stabilities are examined using the density functional theory (DFT) computation. Both frameworks are constructed by connecting exohedral metallofullerene nodes with conjugated organic linkers, akin to the common metal–organic framework (MOF). The DFT calculations suggest that hydrogen molecules can be adsorbed in the frameworks with the hydrogen binding energies ranging from 0.15–0.50 eV, satisfying the optimal adsorption condition for hydrogen storage. Moreover, our computation suggests that the frameworks can entail molecular H_2 binding in the range of 8.0–9.2 wt%, meeting the Department of Energy (DOE) target of 2010 or 2015.

Introduction

Hydrogen holds the promise as one of the major energy resources in place of the fossil fuel.[1] For future automobile applications, the US DOE has set the 6.0 wt% and 9.0 wt% on-board hydrogen storage capacity as targets for the year of 2010 and 2015.[2] To date, a material with high gravimetric/volumetric density of hydrogen molecules while being able to operate reversibly under moderate temperature and pressure conditions is still lacking. It is known that storage of hydrogen molecules in either gas or liquid state is undesirable for automobile applications due to either too low volumetric density or the prerequisite of high-energy cost for hydrogen liquefaction. Hence, seeking ideal solid-state hydrogen-storage materials has been a central focus of recent research. Today, metal/complex hydrides and nano-structured materials have been widely viewed as two most promising solid materials for hydrogen storage.[3–14] High gravimetric density (>10 wt%) can be easily achieved for solids containing only light elements such as Li, Be, B, C, Na, Mg, and Al. One subtlety of utilizing metal/complex hydrides is that hydrogen is stored either in the form of strong covalent bond or ionic bond, while a subtlety of using nano-structured materials is that hydrogen is stored in the form of weakly van der Waals (vdW) bond. Thus the stored hydrogen would be either very difficult to desorb or too easy to desorb at low temperature. Although notable progress has been made towards meeting the DOE's targets for hydrogen storage, the ideal storage system is yet to be synthesized.

The optimal H_2 adsorption energy is in the range of 0.2–0.6 eV per H_2 for retrievable storage and kinetic requirement in ambient condition.[15,16] Some early experiments have shown that pristine carbon nanotubes can store hydrogen but with only limited capacity.[17–19] Further experiments shown the addition of transition metal could enhance binding energies for non-dissociative hydrogen adsorption on single-walled (~20 kJ mol^{-1}) and multi-walled carbon nanotubes (~54 kJ mol^{-1}).[20,21] The hydrogen binding energies are significantly stronger than vdW interaction between H_2 and the carbon nanotubes, but much less than the chemisorption energy of the atomic hydrogen. Recently, some theoretical studies predicted a number of organometallic carbon fullerenes and nanotubes as potential hydrogen storage materials. Sun *et al.* employed DFT and investigated the interaction between the hydrogen and Ti-coated fullerenes. They showed that Ti tends to form metal clusters on the fullerene surface rather than to cover the surface uniformly. Such a clustering tendency prevents Ti being an effective covering element on fullerenes for binding hydrogen molecules.[22] Later, Sun predicted that a buckyball C_{60} can be coated with twelve Li atoms on which total $60H_2$ can be adsorbed with the adsorption energy of 0.075 eV per H_2.[23] More importantly, they showed that the uniformly Li-coated fullerene is energetically more favorable than the fullerene combined with a Li-cluster. Zhang and co-workers investigated hydrogen storage capability of TM-coated C_{60} and $C_{48}B_{12}$ fullerenes. They predicted that the maximum reversible hydrogen storage in these systems can be as high as 9 wt%.[21] Wu *et al.* suggested that Li-coated boron carbide nanotubes could store H_2 with more than 6 wt% and with the binding energy in the range of 10–24 kJ mol^{-1},[24a] and so could the edge-modified graphene nano-ribbons with Sc.[24b] Sun *et al.* also suggested that Li-coated and

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B-doped heterofullerene ($Li_{12}C_{48}B_{12}$) could store hydrogen up to 9 wt%.[25a] Some recent theoretical studies by Yoon *et al.*[25b] and Wang *et al.*[26] suggested that the Ca-coated fullerenes can reach the hydrogen uptake of 8.4 wt%, close to the DOE 2015 target.

We also note that metal–organic framework (MOF) systems have attracted much attention due to their relatively high hydrogen uptake at low temperature.[10,11] For example, isoreticular metal–organic framework-1 (IRMOF-1) can store 1.3 wt% hydrogen, and isoreticular metal–organic framework-11 (IRMOF-11) can store 1.6 wt% hydrogen at 77 K.[27] At room temperature and pressure of 10 bar, hydrogen uptake of 2 wt% has been detected for the isoreticular metal–organic framework-8 (IRMOF-8).[10] It has also been reported that metal–organic framwork-5 (MOF-5) can adsorb up to 4.5 wt% hydrogen at 78 K but only 1 wt% at the room temperature and 20 bar. Another experiment demonstrates that the adsorption of hydrogen in MOF-177 and IRMOF-20 saturates between 70 and 80 bar, within which the H_2 uptake can be as high as 7.5 and 6.7 wt%, respectively.[28] Dincă *et al.* reported a novel MOF with exposed Mn^{2+} coordination sites and a previously unknown cubic topology.[29] This MOF is capable of H_2-uptake of 6.9 wt% at 77 K and 90 bar. Lastly, the covalent-organic frameworks synthesized in Yaghi group can provide more flexible options as hydrogen storage systems.[30]

Although MOF is a promising candidate for hydrogen storage, their adsorption capacities are yet to meet the DOE targets for practical applications. To improve the hydrogen binding capability, Yang *et al.* introduced Li-cations in the anionic MOF built from In(III) center and tetracarboxylic acid ligands, and they found enhanced H_2 adsorption as well as an increase in the isosteric heat of adsorption.[31] Yaghi and co-workers synthesized MOF materials with ultrahigh porosity[32] and large-pore apertures[33] to further increase the hydrogen-storage capacity. Meanwhile, Bacsa *et al.* designed several fullerene-based MOF materials.[34] Very recently, Rao *et al.* suggested encapsulated buckyballs in the cavity of Li-doped MOF and predicted ultra-high H_2 uptakes at room temperature.[35] Han and Goddard also predicted that the Li-doped MOF can lead to a gravimetric H_2 uptake of 6.0 wt% which just meets the 2010 DOE target.[36]

In this article, we present a new design strategy to combine advantages of both hydrogen-storage nanomaterials and MOF. Specifically, we propose two new frameworks, one three-dimensional (FW-1) and one two-dimensional (FW-2), with the exohedral metallofullerenes as nodes and organic molecules as linkers. Based on DFT calculations, we find that both FW-1 and FW-2 could store H_2 above 8.0 wt%, which meets the 2010 DOE target.

Computational methods

The first framework, FW-1 (see Fig. 1), is composed of $Li_8@C_{48}B_{12}$ nodes and Li-doped benzenedicarboxylate (BDC) linkers. The second framework, FW-2, is a 2D network which is built upon the $Ca_{32}C_{60}$-node and *p*-dihydroxybenzene linker (see Fig. 2). FW-1 and FW-2 possess cubic and hexagonal unit cells, respectively. For FW-2, the distance between sheets is set as 15 Å, which is large enough to neglect interactions among periodic images. All geometries are optimized and the lattice is relaxed using LDA-PWC[37] and GGA-PBE[38] DFT method, respectively. Both LDA-PWC and GGA-PBE methods are also employed to compute the H_2 binding energies on the MOF fragments systematically. The values obtained can be viewed as the lower-limit and upper-limit of the H_2 binding energies.[39] Furthermore, Grimme dispersion correction (D_2) is used to evaluate weak interactions,[40] and to compare with LDA and PBE calculations. Semi-core pseudo-potential is used together with the double numerical plus polarization basis set (DNP).[41] The SCF convergence is set as 10^{-5} Hartree. The global orbital cutoff is 4.80 Å. The energy threshold for geometry optimization is 2×10^{-5} Hartree. All calculations are carried out using the Dmol3 software package.[41] The binding energies between H_2 and frameworks are defined as $\Delta E_{binding}/H_2 = (N_{H_2} \times E(H_2) + E(FW) - E(N_{H_2} - FW))/N_{H_2}$.

Results and discussion

H_2 molecules are introduced one by one into the supercell of the framework FW-1. The maximum number of H_2 adsorbed on each Li and oxygen atom is three and two, respectively. It was suggested that Li^+ ion could bind up to six H_2 molecules with the binding energies in the range of 0.202 to 0.253 eV per H_2.[42] However, the neutral Li atoms on fullerenes can adsorb up to three H_2 molecules due to the lack of the positive charge.[25a] Hence, the maximum H_2 loading per supercell is up to $66H_2$ molecules (see Fig. 3). The cell length and corresponding H_2 binding energies of system **1** are collected in Table 1. Based on the DFT-PWC calculations, the optimized unit-cell length (17.60 Å) at low hydrogen loadings is slightly longer than that (17.55 Å) without the hydrogen adsorption. On the other hand, all DFT-PBE results give the same optimized unit-cell length (17.80 Å). The distances between an H_2 molecule and Li atom are within 2.10 Å based on LDA-PWC calculation, and 2.30 Å based on GGA-PBE calculation. Similarly, the distance between H_2 and the O atom are shorter than 2.80 Å based on LDA-PWC

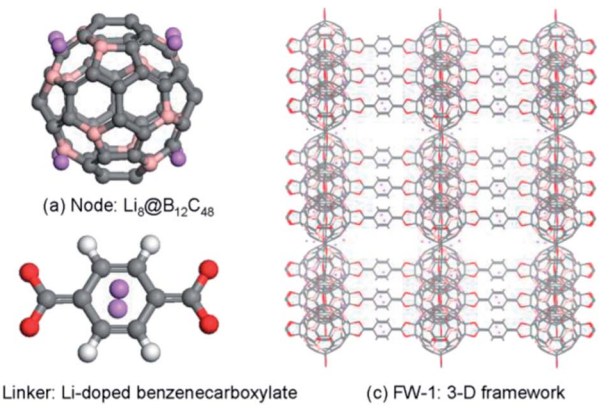

Fig. 1 (a) Node: $Li_8@C_{48}B_{12}$. (b) Linker: Li-doped benzenedicarboxylate. (c) 3-D organic framework constructed by $Li_8@C_{48}B_{12}$ and Li-doped benzenedicarboxylate linker, names as FW-1. Red: oxygen; grey: carbon; white: hydrogen; purple: lithium.

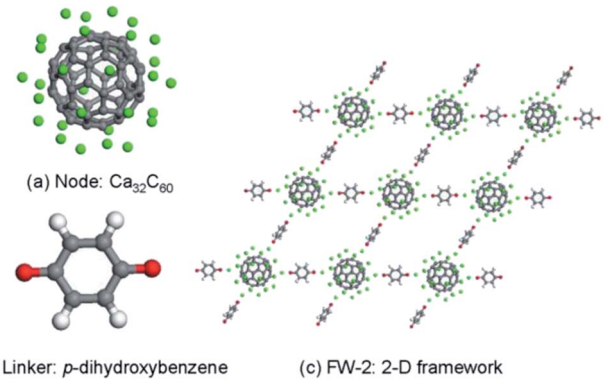

Fig. 2 Optimized structure of (a) node: $Ca_{32}C_{60}$; (b) linker: *p*-dihydroxybenzene. (c) 2-D film constructed by $Ca_{32}C_{60}$ and *p*-dihydroxybenzene, named as FW-2. Red: oxygen; grey: carbon; white: hydrogen; green: calcium.

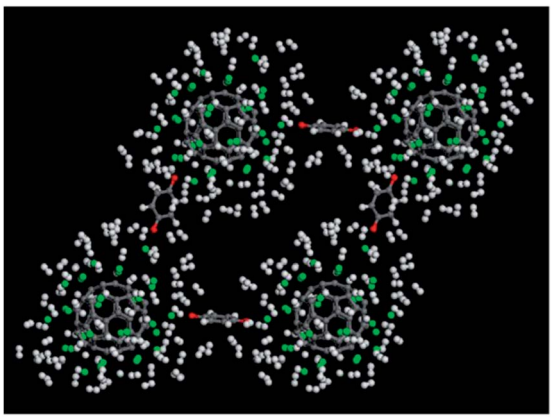

Fig. 4 Optimized structure of $96H_2$–$Ca_{32}C_{60}$ 2-dimensional framework (FW-2).

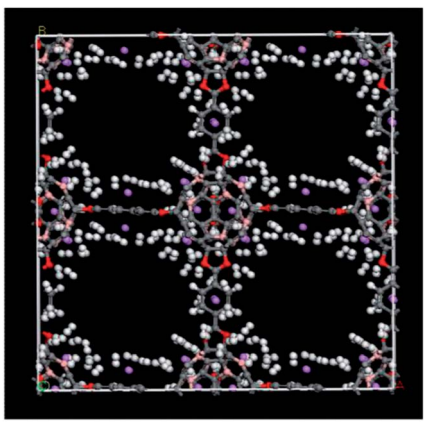

Fig. 3 Optimized structure of the Li-coated $C_{48}B_{12}$ fullerene framework (FW-1) with $66H_2$ adsorbed within the supercell.

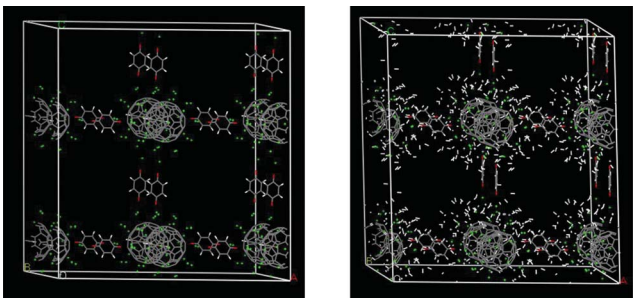

Fig. 5 Optimized structures of $Ca_{32}C_{60}$ and $96H_2$–$Ca_{32}C_{60}$ 3-dimensional framework based on FW-2.

calculation, and 3.20 Å based on GGA-PBE calculation. Meanwhile, the H–H bond lengths are also elongated from 0.764 Å to 0.780 Å based on LDA-PWC calculations, and from 0.751 Å to 0.755 Å based on GGA-PBE calculations. These results indicate that hydrogen molecules interact with Li atoms or oxygen atoms *via* vdW interactions. The binding-energy ranges from 0.20 eV per H_2 to 0.26 eV per H_2 from DFT-PWC calculations, greater than that from DFT-PBE calculations (0.07 eV per H_2 to 0.14 eV per H_2). These values are nearly the same as previously reported DFT results of the H_2 binding energy on the Li-doped boron carbide nanotubes (GGA-PBE: 0.084 eV per H_2; LDA-PWC: 0.196 eV per H_2)[24] and on fullerenes (GGA-PW91: 0.075 eV per H_2).[23] Considering that the H_2 binding energies on MOF materials are underestimated by GGA-PBE calculations but slightly overestimated by LDA-DFT.[21b,34,39] The binding energies between H_2 and FW-1 framework are likely in the range of 0.10–0.20 eV per H_2, which could be further confirmed by the PBE-D results with the binding energy of 0.19–0.29 eV per H_2. With full H_2 loading, the FW-1 can adsorb 9.2 wt% H_2, satisfying the DOE's criteria.

The hydrogen-storage capacity of $Ca_{32}C_{60}$ was reported by Yoon *et al.* recently.[43] Their studies suggest that Ca is superior to

Table 1 Optimized unit length (Å) of Li-coated $C_{48}B_{12}$ fullerene organic framework FW-1 with and without H_2 adsorption, and the computed binding (adsorption) energy/H_2 (eV)

	LDA-PWC		GGA-PBE		PBE-D
	Unit length (Å)	$\Delta E_{binding}/H_2$ (eV)	Unit length (Å)	$\Delta E_{binding}/H_2$ (eV)	$\Delta E_{binding}/H_2$ (eV)
$0H_2$	17.60		17.80		
$14H_2$	17.60	0.26	17.80	0.14	0.29
$28H_2$	17.60	0.25	17.80	0.12	0.28
$42H_2$	17.55	0.23	17.80	0.10	0.23
$54H_2$	17.55	0.21	17.80	0.08	0.21
$66H_2$	17.55	0.20	17.80	0.07	0.19

other metal elements and the hydrogen uptake can be >8.4 wt%. Here, we use $Ca_{32}C_{60}$ clusters to replace metal center of a MOF to construct a 2-D film (Fig. 2c). The *p*-dihydroxybenzene is used as a linker to connect neighbouring $Ca_{32}C_{60}$ clusters. The Ca–C bond length is in the range of 2.64 Å – 3.27 Å based on LDA-PWC calculations and 2.73 Å – 3.12 Å based on GGA-PBE calculations, respectively. The Hirshfeld charge analysis shows that Ca atoms carry an average positive charge of 0.19 |e|. This charge indicates that the adsorption of H_2 on Ca atoms are mainly owing to a polarization mechanism.[43] The average Ca–O bond length is 2.02 Å (LDA-PWC) and 2.05 Å (GGA-PBE), for which the average binding energy between *p*-dihydroxybenzene linker and $Ca_{32}C_{60}$ is 2.73 eV and 2.40 eV, respectively. Such a strong binding suggests the network structure of FW-2 is stable. With total 96 hydrogen molecules ($3H_2$ molecules/Ca) loaded into the supercell, the computed average hydrogen binding energy is 0.57 eV per H_2 and 0.25 eV per H_2, respectively, based on LDA-PWC and GGA-PBE calculations. Similarly, the PBE-D calculation gives the binding energy of 0.31 eV per H_2. These hydrogen binding-energy values are consistent with previous results, indicating favourable H_2 adsorption in the FW-2 system. At the maximum loading (Fig. 4), the H_2 gravimetric density is >8.0 wt %, meeting the DOE 2010 target.

In addition to the layered structures based on FW-2 system, we also design a 3-dimensional network system based on FW-2 (shown in Fig. 5). The PBE-D calculation indicates the average hydrogen binding energy is 0.35 eV per H_2 ($96H_2$ per $Ca_{32}C_{60}$), close to that for the FW-2 system. The 3-D network is expected to provide a more suitable medium for hydrogen-storage applications.

Conclusion

In conclusion, two microporous frameworks consisting of organic linkers and exohedral metallofullerene nodes are designed as potential hydrogen storage materials. Both frameworks are predicted to be mechanically stable based on DFT computations. Importantly, both frameworks can store H_2 with a gravimetric density up to 8–9.2 wt% and with the hydrogen binding energy of 0.15–0.25 eV per H_2 and 0.30–0.50 eV per H_2, respectively. These energy values lie within the optimal range of H_2 adsorption energy for hydrogen storage. The weight percentages also meet the DOE target of 2010 or 2015. The fundamental chemical mechanism underlying the framework design may be exploited for ultimate realization of an ideal hydrogen storage material for automobile application.

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