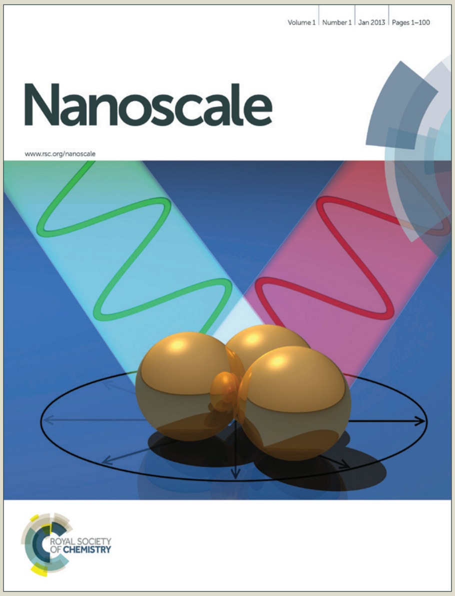
Nanoscale

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/nanoscale

“H_2 sponge”: Pressure as a means for reversible high-capacity hydrogen storage in nanoporous Ca-intercalated covalent organic framework

Fei Gao[1], Jia Tao Sun[1], Sheng Meng[1,2]
[1]Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[2]Collaborative Innovation Center of Quantum Matter, Beijing 100190, China

Abstract: We explore the potential and advantages of Ca-intercalated covalent organic framework-1 (CaCOF-1) as a 3-dimensional (3D) layered material for reversible hydrogen storage. Density functional theory calculations show that by varying the interlayer distance of CaCOF-1, a series of metastable structures can be achieved with the interlayer distance falling in the range of 4.3 ~ 4.8 Å. When four hydrogen molecules are adsorbed on each Ca, a high hydrogen uptake of 4.54 wt% can be produced, with the binding energy falling in the ideal range of 0.2-0.6 eV/H_2. While H_2 absorption is a spontaneous process under H_2 rich conditions, tuning the interlayer distance by reasonable external pressure could compress CaCOF-1 to release all of hydrogen molecules and restore the material to its original state for recyclable use. This provides a new way for gradual, controllable extraction of hydrogen molecules in covalent organic frameworks, satisfying practical demand for reversible hydrogen storage at ambient temperatures.

I. Introduction

Owing to its abundance, intensive energy capacity, and environmental friendliness, hydrogen is viewed as an appealing energy carrier alternative to fossil fuels in many applications [1, 2]. A wide range of materials are currently being considered as potential reversible hydrogen media [3-7]. Identifying new efficient and portable storage materials has been, however, the major challenge for the advancement of hydrogen technology because of the lack of safe, economical and efficient matrix materials of storing and extracting molecular hydrogen at or near room temperature.

In general, a hydrogen molecule could be hosted in matrix materials in two ways, physisorption and chemisorption. In the first case, the matrix materials cannot adsorb enough hydrogen because of too weak binding between H_2 and substrates; whereas in the other case, H storage density is largely enhanced thanks to strong chemical interactions, but the release of hydrogen becomes difficult with hydrogen stored mostly in atomic forms. Consequently, most pure carbon-based porous nanomaterials [3-5], such as fullerene, nanotube, covalent organic frameworks (COFs), failed to store H_2 at room temperature and ambient pressure, due to weak physisorption. While a few metal media can store a large amount of hydrogen, the bonds of hydrogen molecule are broken to form metal hydrides, which makes the process of releasing hydrogen requires high temperatures (>500 K), and not all of the chemisorbed hydrogen could be extracted. For example, Li_3N can absorb 9.3 wt% hydrogen, but it could only exhibit reversibility at a temperature higher than 230 ℃ and less than 55% hydrogen are desorbed in total [6]. High pressure can be used to improve hydrogen capacity, and reversible hydrogen desorption is achieved when releasing external pressure [8], but containers made of highly durable heavy metals are needed presenting additional sources of cost and risk. The problems of low capacity, high temperature, and high risk persist even with the help of external pressure. The search for a matrix material suitable for the hydrogen adsorption and extraction with an intermediate coupling at ambient conditions is of utmost importance.

It is demonstrated that the ideal energy range for hydrogen binding is 0.2 to 0.6 eV/H_2 to favor ambient condition hydrogen storage/release processes [9, 10]. Although many great efforts have been reported, such as doping light metals into porous networks and substituting carbon atoms by boron or nitrogen atoms [11-14], a high H adsorption capacity with high retrievability at near ambient conditions is not achieved. For example, Ca-decorated B-doped COFs were predicted to absorb up to 6.5 wt% hydrogen, but the high capacity can be maintained only at a low temperature due to small adsorption energy and it is hard to fabricate such materials in reality [15]. It has become a primary challenge to find a new material or a new way, which could adsorb and release hydrogen efficiently in near ambient conditions.

In this work, we report an interesting new phenomenon for high capacity reversible H_2 storage in novel 3-dimensional (3D) layered materials. Ca-intercalated covalent organic framework-1 (CaCOF-1) can spontaneously adsorb ~5 wt% H_2 molecules with an ideal binding energy, and more importantly, all these H_2 can be gradually released under compressive external pressure applied to the solid absorbent (see FIG. 1). In CaCOF-1, Ca plays a central role, which spontaneously binds four hydrogen molecules each leading to the increased layer separation of CaCOF-1 from 4.3 to 4.8 Å. Meanwhile, when the layer separation of CaCOF-1 is decreased by the applied compressive pressure, the binding energy of molecular H_2 gradually decreases and the extraction of molecular H_2

can be easily achieved. This exemplifies a new approach to compress solid adsorbent materials for H_2 extraction, in the same way as squeezing wet sponges to produce fresh water, which is radically distinct from traditional methods where high pressure in a heavy durable metal tank is used to enhance hydrogen capacity. Strikingly, CaCOF-1 could release all of adsorbed hydrogen resulting a 4.54 wt% H_2 extraction and return to its original state for recyclable usage. This proposal demonstrates a controllable way for practical hydrogen storage and extraction at near ambient conditions.

II. Methodology

Our first-principles calculations are performed within the framework of density functional theory (DFT) using Vienna Ab initio Simulation Package (VASP) [16]. The ultrasoft pseudopotentials [17, 18] and the gradient generalized approximation (GGA) in the Perdew-Wang form [19] for exchange-correlation energy are used for optimizing the crystal structure and calculating external pressure. We also employ local density approximation (LDA) [20] calculations for comparison. Although GGA tends to underestimate H_2 binding energy and LDA overestimate it, the trends for comparing relative energy differences should be reliable [21, 22]. The van der Waals density functional (vdW-DF) recently developed by Langreth et al. [23] and parameterized by Klimes et al. [24] is also employed to check the relative energies. Spin polarization is invoked whenever necessary. A plane wave cutoff of 400 eV is used to expand the wave function and the total energy is converged to a level of 0.0001 eV during the self-consistent electron density optimization. All atoms are allowed to relax until the forces on each atom have magnitudes less than 0.01 eV/Å. The Brillouin zone was sampled using the Monkhorst-Pack scheme with a 1×1×3 for GGA and LDA, and 1×1×5 for vdW-DF calculations. The convergence test for denser K-point sampling (1×1×7) has been performed which shows the total energy variation is less than 0.001 eV/atom.

III. Results and Discussion

In recent experiment, 2-dimensional (2D) COF-1 has been successfully synthesized by dehydration reaction of 1, 4-benzenediboronic acid. This material consists of 18 carbon atoms, 12 hydrogen atoms, 6 oxygen atoms and 6 boron atoms in one unit cell. Then 3D COF-1 is built by the B_3O_3 rings in one layer connected to the C_6H_4 rings in the neighboring layer with lattice parameters: $a = b = 15.420$ Å and $c = 6.655$ Å [25]. Based on this knowledge, a newly 3D Ca- intercalated compound, CaCOF-1, has been designed, which is formed by stacking planar COF-1 layers and intercalated Ca atoms, as shown in FIG. 2 [26]. The lattice constants for minimum energy ground-state configuration are obtained: $a = b = 15.20$ Å and $c = 4.4$ Å. The bond lengths of B-C and B-O are 1.52 and 1.39 Å, meanwhile the angles of B-O-B and O-B-O are 120.9° and 119.0°, respectively. Most of structural parameters in CaCOF-1 are similar to those in COF-1, except the layer separation (L). Due to the presence of the Ca atoms, the layer separation of CaCOF-1 is 4.4 Å, and it is about 3.3 Å in COF-1. We also notice that, in CaCOF-1, Ca binding energy E_{Ca} is 2.93 eV/Ca, significantly exceeding the cohesive energy of $E_{\mathrm{c}} = 1.88$ eV for bulk Ca using GGA. Here, the binding energy (E_{Ca}) of the intercalated Ca atom in CaCOF-1 is defined as follows:

$$E_{Ca} = \frac{E_{CaCOF-1} - E_{COF-1} - nE_{atom\,Ca}}{n} \qquad (1)$$

Here n is the number of Ca atoms in CaCOF-1 and $n = 3$ for each unit cell.

And the cohesive energy for bulk Ca (E_{c}) is defined as follows:

$$E_c = \frac{E_{bulk\,Ca} - nE_{atom\,Ca}}{n} \qquad (2)$$

Here n is the number of Ca atoms in the supercell calculations of bulk Ca.

Furthermore, when layer separation falls in the range of 4.0 ~ 5.0 Å, the binding energies of Ca are all larger than 1.88 eV. That means the porous nanomaterial is relatively stable and could keep the crystal structure in this range. When the van der Waals dispersion force is included, the binding energy increases to 3.37 eV and the interlayer distance turns 4.3 Å using vdW-DF; the additional 0.44 eV is attributed to the vdW interactions between COF-1 layers. We expect Ca-intercalated COF-1 to be experimentally fabricated via self-assembly of nanoscale components including benzene diboronic acid building blocks or by Ca intercalation between weakly bound COF-1 layers at high temperatures in inert gases.

The proposed CaCOF-1 is a nanoporous material with a high density of pores of diameter of 1.5 nm, a key feature essential for H_2 storage, which provides barrierless diffusion channels for charging and discharging cycles. As a result, layered material CaCOF-1 has an intrinsic advantage for hydrogen storage, with the gravimetric density reaches 4.54 wt% [26]. In the process of adsorbing four hydrogen molecules per Ca atom, the layer separation of CaCOF-1 is increased from 4.3 to 4.8 Å using vdW-DF (4.4 to 4.9 Å in GGA) during geometry optimization, and the total energy is lowered by 2.16 eV per unit cell with respect to clean CaCOF-1 and isolated H_2 molecules, as shown in FIG. 3a and FIG. 4. Here, long range interaction should not be neglected, and the binding energy of H_2 molecule adsorbed (E_b) in CaCOF-1 is defined as follows:

$$E_b = \frac{E_{nH_2-CaCOF-1} - E_{CaCOF-1} - nE_{H_2}}{n} \qquad (3)$$

A more negative value E_b indicates a stronger binding between the hydrogen molecules and CaCOF-1. By using vdW-DF, the average binding energy of per H_2 molecule is -0.18 eV/H_2, which is a reasonable value lying between GGA (−0.077 eV/H_2) and LDA (−0.419 eV/H_2) results respectively. All bonds of H_2 are parallel with the plane of COF-1 layer, and hydrogen prefers to be adsorbed at 45° or 135° orientations with respect to the lattice vector in fully optimized geometry, thanks to the charge redistribution of Ca atom in the system. Extensive Bader charge analysis indicates that the positive charges on Ca in the clean CaCOF-1 gradually increase from +1.42|*e*| to +1.46|*e*| when the interlayer distance changes from 4.4 to 4.9 Å (see ESI). Increased positive charges on Ca ion lead to a stronger H_2 binding energy. Upon H_2 adsorption the variation in positive charges on Ca is flattened, yielding a value of ~1.42±0.01|*e*| for interlayer distance changing from 4.4 to 4.9 Å.

To gain a deeper insight of hydrogen storage, two layer separations, 4.3 and 4.8 Å, are tested when a H_2 approaching to the intercalated metal atoms, shown in FIG. 4. It is surprising that only at 4.8 Å that H_2 molecule could be *chemically* trapped, with binding energy 0.08 eV higher than that at 4.3 Å. Energy minima at a large H_2-Ca separation of 4.0 Å is due to weak physical adsorption. This confirms that the interlayer distance of CaCOF-1 determines the adsorption of hydrogen molecules, and the process of increasing layer separation with hydrogen storage is spontaneous. This means the adsorption process is exothermic without an energy barrier and the desorption barriers lying around 0.1-0.2 eV. More interestingly, the larger layer separation produces the higher binding energy of hydrogen molecules (FIG. 3b). When the interlayer distance becomes 5.0 Å, the binding energy is enhanced to −0.21 eV/H_2. The similar dependence of binding energy on the interlayer distance has been observed in graphitic structures [27]. Furthermore, if the layer separation is enlarged, more hydrogen molecules can be trapped between COF-1 layers leading to a higher hydrogen capacity.

This phenomenon inspires us that the release of hydrogen molecules could be achieved via decreasing the layer separation. We compress under a uniaxial pressure the interlayer distance of H_2 adsorbed CaCOF-1 (H_2-CaCOF-1) by reducing the interlayer distance of 0.1 Å each time. It is found that hydrogen adsorption energy becomes smaller consistently and turns positive when the interlayer distance L is smaller than 4.4 Å. The obtained binding energy, 0.02 eV, is low enough for desorption of hydrogen molecules, as shown in FIG. 5. Furthermore, the process for the release of molecular hydrogen could be divided to three steps: I) four hydrogen molecules are bonded to each Ca atom, when L is in the range of 4.8 ~ 5.0 Å; II) around 33% hydrogens are extracted with L from 4.7 to 4.5 Å; Ш) all of molecular H_2 are released when L below 4.4 Å (FIG. 5). The dependence of the binding energy of molecular hydrogen presented here differs from the common view that larger external pressure tends to bind molecular hydrogen more strongly in conventional matrix materials for hydrogen storage.

To regulate hydrogen binding energy via compression of the layer separation in practice, we consider applying a suitable external pressure to hydrogenated CaCOF-1. The applied pressure can be estimated directly by VASP calculation (method *1*) or by fitting the total energy $E(V)$ as a function of volume V through $P(V) = -d\big(E(V)\big)/d(V)$ (method *2*) [27]. Here we use both of them for clean CaCOF-1 when necessary for comparison and GGA calculations are shown to give a good reliability (see in ESI). At L = 4.4 Å, the pressure is around 0 GPa, which means it is the most stable structure for CaCOF-1. Reducing the interlayer distance, the pressure is positive; in contrary, the negative pressure displays that CaCOF-1 is prone to be elongated along the z-direction, the direction normal to COF plane. Moreover, near the equilibrium position, ~4.4 Å, the values produced by the two methods are very close to each other and the greater deviation shows up only made when the system is far away from the stable condition. In spite of that, the two methods yield a similar magnitude of slope around 2 ~ 3 GPa/ Å by linear fitting. We adopt method *1* to obtain pressure values directly from VASP calculations in the following. In FIG. 5, it is clear that *P(V)* shows a nonmonotonic dependence behavior on the interlayer distance. A rather good linear dispersion between external pressure and the interlayer distance of CaCOF-1 is exhibited for each stage. The same as that for CaCOF-1, the positive values means the matrix material is compressed. The most stable structure with a Ca atom binding four hydrogens in CaCOF-1 can be achieved when the pressure goes to zero with L_0 = 4.9 Å. Changing the interlayer distance of 0.1 Å each time, one needs 0.328, 0.332, 0.307 GPa, respectively, for the three H_2 release stages as defined before. If the layer separation of H_2-CaCOF-1 is reduced by 0.2 Å from the equilibrium position (L_0 = 4.9 Å), 33% hydrogen molecules can be extracted by a reasonable pressure of about 0.6 GPa, and the system reaches a new equilibrium with zero pressure after 33% H_2 desorption. Since we use a very small primitive cell and a limited number of H_2 molecules in current calculations, a much smaller pressure might be required in practice if macroscopic materials and statistical processes are taken in account. Afterwards, when a pressure is further applied, all of remaining hydrogen molecules could be recycled. Furthermore, if all H_2 molecules are desorbed, the system would switch into a new equilibrium state with the pressure approaching 0 GPa. When CaCOF-1 is given a reasonable pressure at the beginning, releasing all stored hydrogen molecules steadily at a time is possible and CaCOF-1 can restore to its original state for recyclable use. Only a negligible energy of ~0.011 eV/Ca is needed to compress the CaCOF-1 layer separation by 0.2 Å to release at least one H_2/Ca, which produces the energy of 2.5 eV upon ignition.

To gain a further understanding, molecular dynamics (MD) simulations on the process of H_2 storage and release are performed. In the MD simulations using LDA exchange-correlation functional, the most stable structure with four H_2 adsorbed on each Ca atom in CaCOF-1 at L = 4.8 Å keeps its optimized geometry at 77 and 300 K, and the system will release three out of twelve (~25%) H_2 molecules when the temperature is increased to 400 K. Moreover, at L = 4.3 Å, hydrogen molecules are extracted gradually and all hydrogen can be released at the room temperature after 600 fs (see ESI).

Releasing hydrogen by external pressure is different from conventional methods and has two major advantages: easy control and safety. In general, high gaseous pressure is used to improve H_2 adsorption capacity, and H_2 release is achieved by heating to high temperature, which consumes a large amount of stored energy. Moreover, compressing gaseous hydrogen by pressure or extracting hydrogen by heating are hard to control and especially dangerous, which could lead to an explosion. The method presented in this work gets around these problems by releasing molecular hydrogen in a more efficient and safe way.

IV. Conclusions

In summary, the layered structure CaCOF-1, namely, covalent organic framework (COF-1) intercalated by Ca atoms, has an outstanding feature, which can be used to efficiently adsorb and release molecular H_2 by tuning interlayer separation. By using first-principles calculation we have found that with four molecular hydrogens adsorbed on each Ca atom, the layer separation of CaCOF-1 increases from 4.3 Å to 4.8 Å (from 4.4 Å to 4.9 Å for GGA), and the crystal structure is preserved. More strikingly, the H_2 binding energy and external pressure show consistent trends in this process. With suitably chosen pressure, a one-time release or gradual release of H_2 molecules up to ~5 wt% could be achieved in CaCOF-1. This proposal demonstrates a new controllable way for practical hydrogen adsorption and extraction. More importantly, this method of binding and releasing H_2 by pressure is not limited to the present system, and it is possible that better layered materials with higher capacity and lower working pressure can also be found in future.

Acknowledgment This work is partially funded by MOST (No. 2012CB921403, No. 2013CBA01600), NSFC (No. 11222431, No. 61306114), "Strategic Priority Research Program (B)" of the CAS (No. XDB07030100), the innovation plan and hundred-talent program of CAS.

References

[1] A. Schlapbach and A. Züttel, Nature **414**, 353 (2001).

[2] B. C. H. Steele and A. Heinzel, Nature **414**, 345 (2001).

[3] O. V. Pupysheva, A. A. Farajian, B. I. Yakobson, Nano Lett. **8**, 767 (2008).

[4] C. Liu, Y. Y. Fan, M. H. Liu, T. Cong, H. M. Cheng, and M. S. Dresselhaus, Science **286**, 1127 (1999).

[5] H. Furukawa and O. M. Yaghi, J. Am. Chem. Soc. **131**, 8875 (2009).

[6] P. Chen, Z. Xiong, J. Luo, J. Lin, and K. L. Tan, Nature **420**, 302 (2002).

[7] Y. Zhao, Y. H. Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. **94**, 155504

(2005).

[8] S. Chan, G. Chen, X. G. Gong and Z.-F. Liu, Phys. Rev. Lett. **87**, 205502 (2001).

[9] P. Chen, X. Wu, and K. L. Tan, Science **285**, 91 (1999).

[10] Y. H. Kim, Y. Zhao, A. Williamson, M. J. Heben, and S. B. Zhang, Phys. Rev. Lett. **96**, 016102 (2006).

[11] Q. Sun, P. Jena, Q. Wang, and M. Marquez, J. Am. Chem. Soc. **128**, 9741 (2006).

[12] M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, and Z. Zhang, Phys. Rev. Lett. **100**, 206806 (2008).

[13] H. Lee, J. Ihm, M. L. Cohen, and S. G. Louie, Phys. Rev. B **80**, 115412 (2009).

[14] X. L. Zou, M. H. Cha, S. Kim, M. C. Nguyen, G. Zhou, W. H. Duan, Jisoon Ihm, Int. J. Hydrogen Energy **35**, 198 (2010).

[15] X. Zou, G. Zhou, W. Duan, K. Choi and J. Ihm, J. Phys. Chem. C **114**, 13402 (2010).

[16] G. Kresse, and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[17] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1999).

[18] G. Kresse, and J. Hafner, J. Phys. Condens. Matter **6**, 8245 (1994).

19] Y. Wang, and J. P. Perdew, Phys. Rev. B **44**, 13298 (1991).

[20] D. M. Ceperley, and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[21] Y. Y. Sun, K. Lee, L. Wang, Y. H. Kim, W.Chen, Z. F. Chen, and S. B. Zhang, Phys. Rev. B **82**, 073401 (2010).

[22] P. Srepusharawoot, R. H. Scheicher, C. M. Araújo, A. Blomqvist, U. Pinsook, and R. Ahuja, J. Phys. Chem. C **113**, 8498 (2009).

[23] M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **92**,

246401 (2004).

[24] J. Klimes, D. R. Bowler, and A. Michaelides, Phys. Rev. B **83**, 1951301 (2011).

[25] A. P. Côté, A. I. Benin, N. W. Ockwig, M. Ô. Keeffe, A. J. Matzger, and O. M. Yaghi, Science **310**, 1166 (2005).

[26] F. Gao, Z. Ding and S. Meng, Scientific Reports **3**, 1882 (2013).

[27] Y. Lei, S. A. Shevlin, W. G. Zhu and Z. X. Guo, Phys. Rev. B **77**, 134114 (2008).

Figures

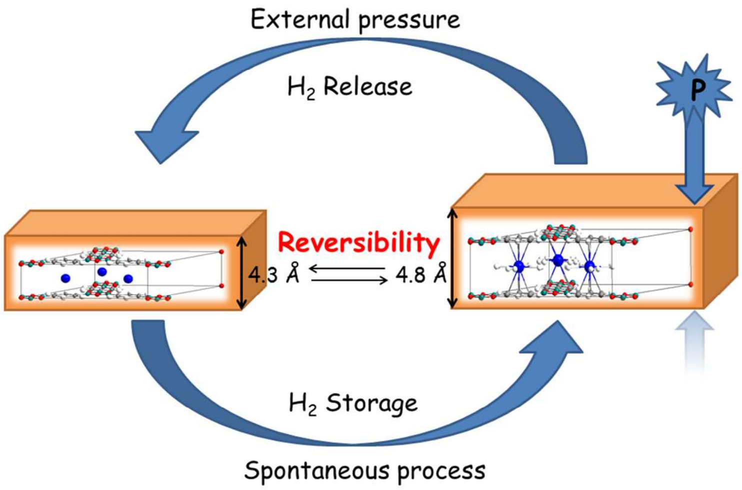


FIG. 1 Schematic diagram showing reversible adsorption and release processes for H_2 in CaCOF-1.

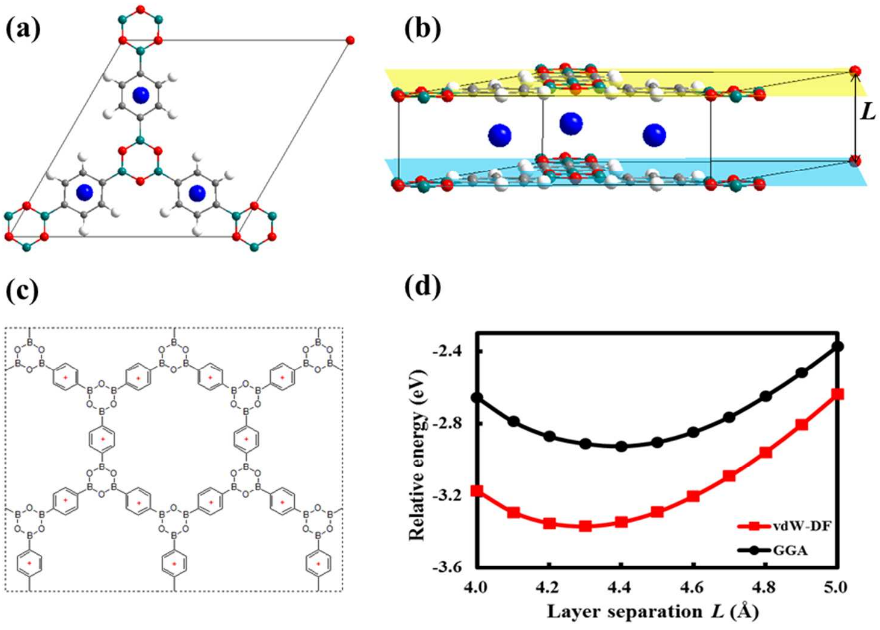


FIG. 2 Formation of CaCOF-1. (a) Top and (b) side view of CaCOF-1 unit cell. Gray, white, green, red and blue spheres represent C, H, B, O and Ca atoms, respectively; (c) top view of 2D extended COF-1. Red daggers mark positions for Ca binding; (d) Ca relative energy as a function of layer separation (L) using GGA functional and vdW-DF.

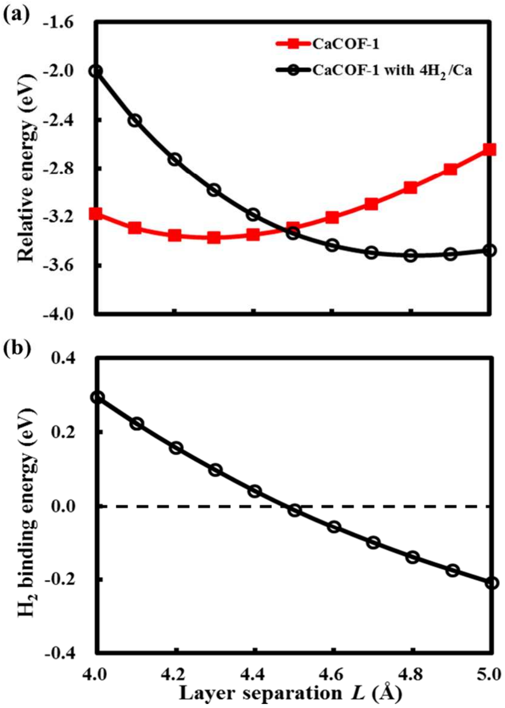


FIG. 3 (a) Relative energy of two cases of CaCOF-1 as a function of the layer separation L calculated with vdW-DF. Red and black lines represent original CaCOF-1 and H_2 adsorbed CaCOF-1. (b) Average H_2 binding energy (E_b) as a function of the layer separation of H_2 adsorbed CaCOF-1 from vdW-DF calculations. A more negative E_b indicates a stronger binding between the hydrogen and CaCOF-1. Black dashed line shows H binding energy is zero.

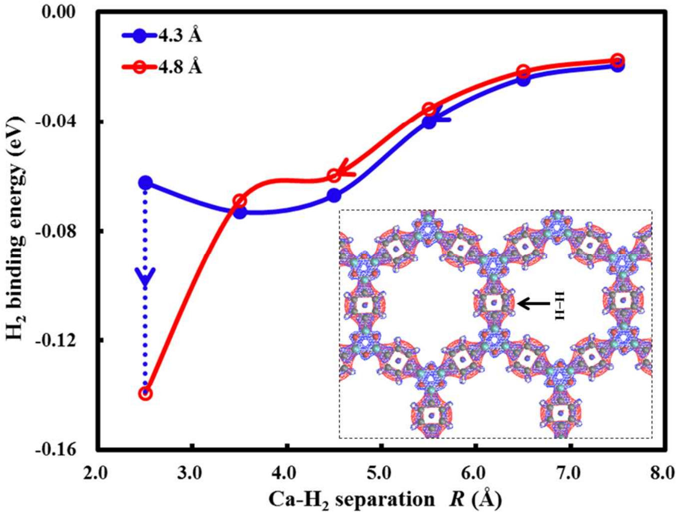


FIG. 4 H_2 binding energy as a function of the distance between Ca and H_2. Red and blue lines represent route for the layer separation of 4.3 and 4.8 Å, respectively. The inset shows the charge density of CaCOF-1. Red and blue clouds correspond to electron depletion and accumulation regions upon Ca binding, respectively.

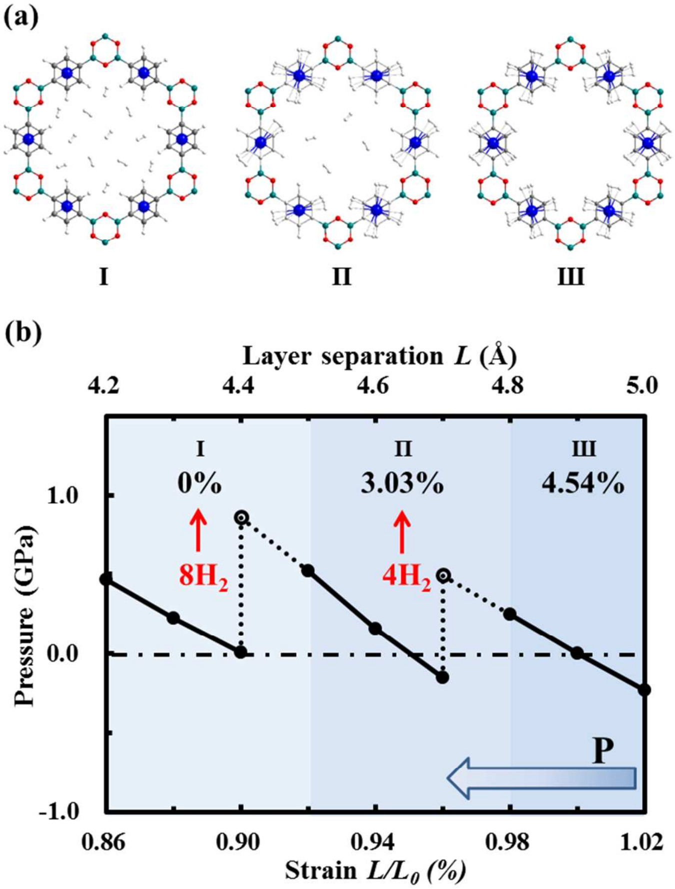


FIG. 5 (a) Top view of H_2-CaCOF-1 for the three stages of hydrogen release. (b) Pressure as a function of the layer distance L for H_2-CaCOF-1. Black dashed line means the pressure is zero and the values of pressure are obtained using VASP. The shaded areas in different colors represent different percentage of hydrogen stored during the three stages. The positive pressure means the material is compressed along the *z*-direction (normal to the COF plane).