

# First-Principles Study of Hydrogen Storage of Sc-Modified Semiconductor Covalent Organic Framework-1

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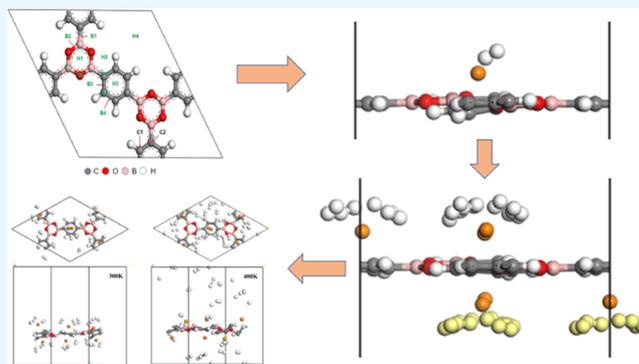
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**ABSTRACT:** At present, the development of new carbon-based nanoporous materials with semiconductor properties and high hydrogen storage capacity has become a research hotspot in the field of hydrogen storage and hydrogen supply. Here, we pioneered the study of the hydrogen storage capacity of a scandium (Sc) atom-modified semiconductor covalent organic framework-1 (COF-1) layer. It was found that the hydrogen storage capacity of the COF-1 structure was significantly enhanced after the modification of the Sc atom. We found that each Sc atom of the modified COF-1 structure can stably adsorb up to four H<sub>2</sub> molecules, and the average adsorption energy of the four hydrogen molecules is  $-0.284$  eV/H<sub>2</sub>. Six Sc atoms are stably adsorbed most bilaterally on the cell of the COF-1 unit, which can adsorb 24 H<sub>2</sub> molecules in total. In addition, we have further studied the adsorption and desorption behaviors of H<sub>2</sub> molecules on the 6Sc-COF-1 surface at 300 and 400 K, respectively. It can be found that each Sc atom of the COF-1 unit cell can stably adsorb three H<sub>2</sub> molecules with a hydrogen storage performance of 5.23 wt % at 300 K, which is higher than those of lithium-modified phosphorene (4.4 wt %) and lithium-substituted BHNH sheets (3.16 wt %). At 400 K, all of the adsorbed H<sub>2</sub> molecules are released. This confirms the excellent reversibility of 6Sc-COF-1 in hydrogen storage performance. This research has great significance in the application of fuel cells, surpassing traditional hydrogen storage materials.



## 1. INTRODUCTION

With the advancement of science and technology and the acceleration of industrialization, the demand for energy in today's society is increasing, and it is important to find sustainable renewable energy. Compared with traditional fossil fuels, hydrogen energy has many advantages, such as high heat generation, rich reserves, and no pollutants. It is an ideal candidate for sustainable energy and renewable energy. So, it can be used as a suitable substitute for fossil fuels.<sup>1,2</sup> A key obstacle for using hydrogen as sustainable energy is its safe and effective storage under environmental conditions. In the past few years, many researchers devoted themselves to study materials that can maintain the high weight and bulk density of hydrogen under environmental conditions. Theoretically, the adsorption energy of hydrogen molecules should be in the range of 0.2–0.4 eV to achieve reversible hydrogen adsorption and desorption.<sup>3–5</sup> Thus, it is better to store hydrogen molecules as solid materials, such as two-dimensional sheetlike materials h-BN,<sup>6</sup> SiC,<sup>77</sup> C<sub>3</sub>N,<sup>8</sup> and BC<sub>3</sub>.<sup>99</sup>

In recent years, with the development of metal–organic frameworks (MOFs)<sup>10</sup> and covalent organic frameworks (COFs),<sup>11–14</sup> hydrogen storage methods based on adsorption have shown good advantages, especially in vehicle applications. MOFs and COFs have a higher internal surface area and

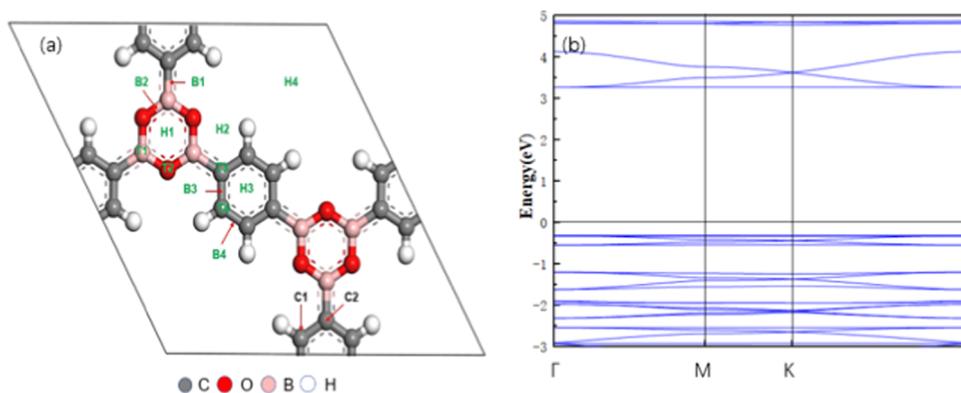
adjustable pore geometry/volume, which makes them attractive in the field of gas storage. Compared with MOFs, COFs have excellent chemical and thermal stability. In addition, they have a regular crystal structure and are composed of lighter elements such as C, H, B, O, etc.,<sup>15–19</sup> which are connected by strong covalent bonds. The first COF structure was prepared by Yaghi<sup>20</sup> through the dehydration condensation of 1,4-benzenediboronic acid ((HO)<sub>2</sub>B-C<sub>6</sub>H<sub>4</sub>-B(OH)<sub>2</sub>) molecules, so it was named COF-1.<sup>20–24</sup> The structure is similar to porous graphene (PG), in which the benzene rings are connected by B<sub>3</sub>O<sub>3</sub>. COF-1 has a pore size of 1.5 nm,<sup>22</sup> which allows it to be used in catalytic materials,<sup>25</sup> membrane materials,<sup>26</sup> and energy storage materials.<sup>27,28</sup> Although the latest research shows that COF-1 has a good hydrogen storage capacity at room temperature,<sup>29</sup> it still cannot achieve the practical application standard at environ-

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**Figure 1.** (a) Top view of the geometric structures of COF-1.  $X_n$  ( $X = \text{H/B/T}$ ,  $n = 1, 2, 3, 4$ ) is possible in high symmetric positions. Red, pink, gray, and white balls represent O, B, C, and H atoms, respectively. (b) Band structures of the pristine monolayer of COF-1 by PBE.

mental temperature stipulated by the US Department of Energy (DOE). To overcome this major drawback, one of the methods is to functionalize COFs with alkali,<sup>30–32</sup> alkaline earth,<sup>33–35</sup> or transition-metal (TM) atoms,<sup>36,37</sup> which are considered to be the binding centers of  $\text{H}_2$  molecules. Recently, Zhao et al.<sup>28</sup> found that three hydrogen molecules were adsorbed around the Li atom in covalent organic framework-1 by Li decorated at 300 K under standard atmospheric pressure, and the hydrogen adsorption performance was 5.26 wt % at room temperature. However, since the interaction between alkali metal or alkaline earth metal atoms and  $\text{H}_2$  molecules is too weak, they are not suitable for hydrogen storage under environmental conditions.<sup>38</sup> Hydrogen molecules are easier to be adsorbed on transition metals (TMs) due to a Kubas-type back-donation effect, in which an s electron of hydrogen is transferred to an empty d orbital of a transition metal and a d electron of a transition metal is transferred to an empty orbital of  $\text{H}_2$  to form an antibonding orbital. Thus, hydrogen molecules adsorbed on TMs are in the intermediate state between physical adsorption and chemical adsorption.<sup>39–41</sup>

The lightest TM atom, Sc, can be used as a dopant to obtain higher hydrogen storage capacity. It has been reported that the theoretical hydrogen storage performance of Sc-modified porous graphene (PG) is 9.09 wt %, and each Sc atom can adsorb five  $\text{H}_2$  molecules, with an average adsorption energy of  $-0.296$  eV.<sup>42</sup> Luo<sup>43</sup> observed that graphene with a three- $N$ -doped single vacancy defect modified by Sc is a good material for hydrogen adsorption with an adsorption energy of 0.2–0.4 eV. The adsorption capacity of  $\text{H}_2$  molecules can be up to 5 wt %. Wu et al.<sup>44</sup> found that Sc-doped 6,6,12-graphene nanotubes (GNs) have a hydrogen adsorption capacity of 5.4 wt %. Also, Ma et al.<sup>45</sup> studied Sc-decorated  $\text{B}_{24}\text{N}_{24}$  and discovered that up to 24  $\text{H}_2$  molecules can be adsorbed around 6 Sc atoms. Ma et al.<sup>46,47</sup> calculated  $\text{C}_{60}$  with defects and  $\text{C}_{24}\text{N}_{24}$  modified by Sc atoms and found that each Sc atom can absorb up to five  $\text{H}_2$  molecules with a storage capacity of 6.80 wt %. The adsorbed  $\text{H}_2$  molecules begin to desorb at 190 K, and all  $\text{H}_2$  molecules are released at 290 K. This implies that the Sc atom plays a very important role in the modification of hydrogen storage materials.<sup>48–50</sup> So far, there are still no research reports on the hydrogen storage performance of COF-1 modified by Sc atoms.

In this work, we study the adsorption capacity of hydrogen molecules on the lightest transition-metal Sc-modified COF-1 structure by first-principles calculations. The results show that

Sc atoms can be stably adsorbed on the COF-1 structure without aggregation and each Sc atom can stably adsorb four hydrogen molecules at 0 K. In addition, we also investigate the adsorption of hydrogen molecules on the two sides of Sc-modified COF-1 and the maximum density of Sc-modified COF-1. Furthermore, an ab initio molecular dynamics (MD) simulation has been carried out to study the adsorption and desorption behaviors of the hydrogen molecules at 300 and 400 K, respectively. It is found that Sc-modified COF-1 is a good reversible hydrogen storage material at room temperature.

## 2. METHOD OF CALCULATION

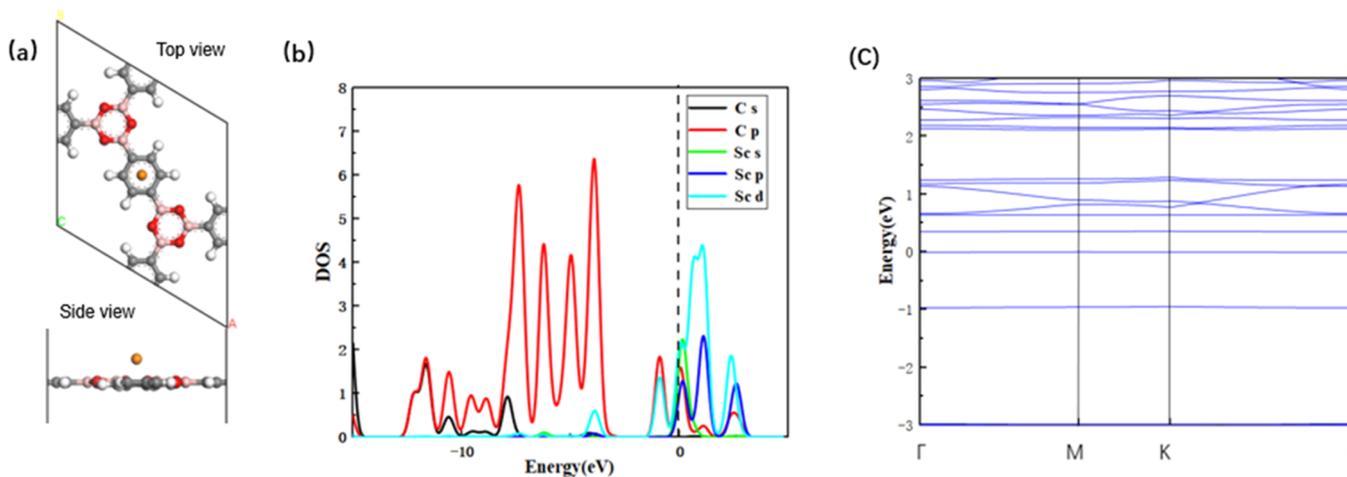
All numerical calculations in this work were based on density functional theory using a CASTEP code.<sup>51</sup> The electronic exchange-correlation function was processed by Perdew, Burke, and Ernzerhof (PBE)'s<sup>52</sup> generalized gradient approximation (GGA).<sup>53</sup> In the case of weaker interactions such as the van der Waals force of hydrogen molecules on the substrate, the use of GGA can reduce the calculation accuracy.<sup>54</sup> So, the Grimme scheme in DFT-D2 correction was used to correct this long dispersion effect.<sup>55</sup> The cutoff energy was set to 500 eV, and the  $k$ -points were set to  $6 \times 6 \times 1$  for all calculations, which is the same as the parameters in the calculation of porous graphene hydrogen storage.<sup>56</sup> The energy of the system was not affected when the cutoff energy and  $k$ -point density were increased, which implied that the parameters chosen were reasonable. To avoid layer-to-layer interaction, the vacuum layer along the C direction was set to 20 Å, the energy convergence standard was set to  $1.0 \times 10^{-5}$  eV, and the convergence of the self-consistent field (SCF) was set to  $2.0 \times 10^{-6}$  eV/atom. All of the atoms of the structure were relaxed after geometry optimization so that the force acting on each atom was less than 0.02 eV/Å.<sup>57</sup>

The binding energy of Sc atoms on the COF-1 structure can be defined by the following equation

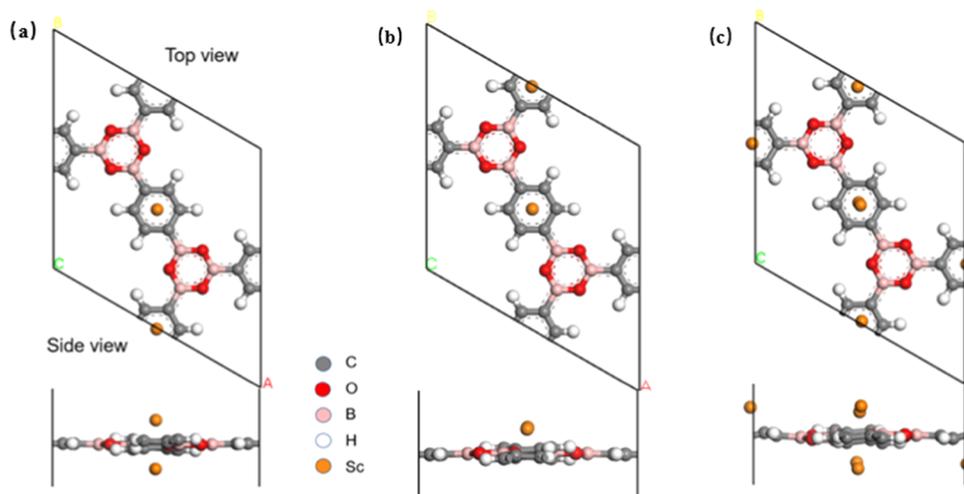
$$E_b = [E_{\text{COF-1+nSc}} - (E_{\text{COF-1}} + nE_{\text{Sc}})]/n \quad (1)$$

where  $E_{\text{COF-1+nSc}}$  and  $E_{\text{COF-1}}$  are the total energies of the  $n$ Sc atom-modified COF-1 structure and the COF-1 system, respectively, and  $E_{\text{Sc}}$  and  $n$  are the energy per Sc atom and the number of metals, respectively.

The adsorption energy ( $E_{\text{ad}}$ ) and average adsorption energy ( $\bar{E}_{\text{ad}}$ ) of adsorbed  $\text{H}_2$  molecules can be circumscribed as follows



**Figure 2.** (a) Optimized structure of Sc-COF-1. (b) DOS of the Sc-COF-1 system. (c) Band structures of the pristine monolayer of Sc-COF-1 by PBE.



**Figure 3.** (a) Two Sc atoms on opposite sides of the COF-1 layer (2Sc-COF-1). (b) Two Sc atoms on the same side of the COF-1 layer (2Sc-COF-1). (c) Six Sc atoms on both sides of the COF-1 layer (6Sc-COF-1).

$$E_{\text{ad}} = E_{m\text{H}_2+n\text{Sc}+\text{COF-1}} - E_{(m-1)\text{H}_2+n\text{Sc}+\text{COF-1}} - E_{\text{H}_2} \quad (2)$$

$$E_{\text{ad}} = [E_{m\text{H}_2+n\text{Sc}+\text{COF-1}} - E_{n\text{Sc}+\text{COF-1}} - mE_{\text{H}_2}]/m \quad (3)$$

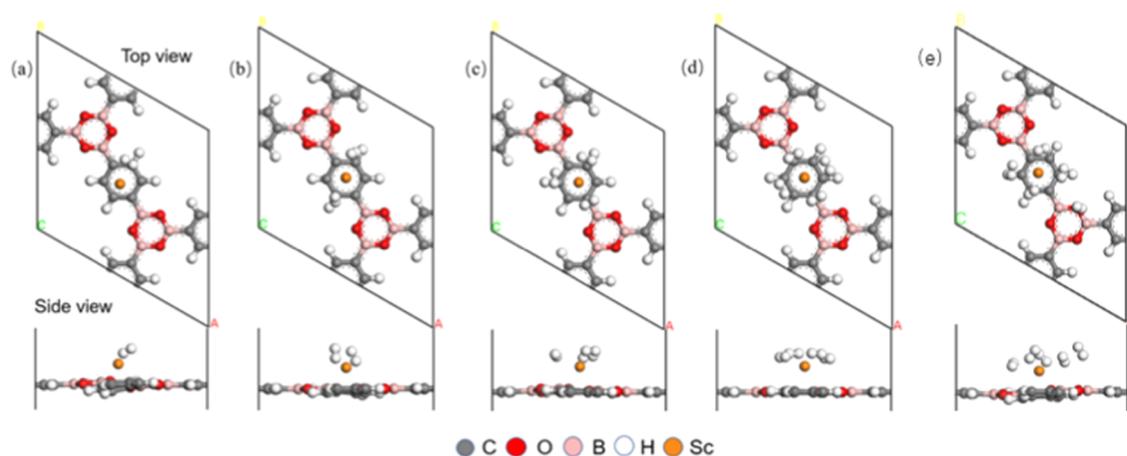
where  $E_{m\text{H}_2+n\text{Sc}+\text{COF-1}}$  and  $E_{(m-1)\text{H}_2+n\text{Sc}+\text{COF-1}}$  are the total energies of the system with  $m\text{H}_2$  molecules adsorbed and  $(m-1)\text{H}_2$  molecules adsorbed, respectively, and  $E_{n\text{Sc}+\text{COF-1}}$ ,  $E_{\text{H}_2}$ , and  $m$  represent the total energy of the  $n\text{Sc-COF-1}$  system, the total energy of a single  $\text{H}_2$  molecule, and the number of adsorbed  $\text{H}_2$  molecules, respectively.

Figure 1a depicts the fully optimized geometry of the COF-1 layer. The calculated lattice constants are 15.11 Å. The bond lengths of C–B and B–O are 1.55 and 1.39 Å, respectively, which are in good agreement with the experimental value ( $a = b = 15.42$  Å)<sup>21</sup> and density functional-based tight-binding (DFTB) calculations ( $a = b = 14.90$  Å).<sup>58</sup> This implies that the model is reasonable. There are two types of C atoms in the COF-1 structure. We define them as C1 and C2. It is found that C1-type atoms connect two carbon atoms and one H atom, while C2 atoms connect two carbon atoms and one B atom. We considered 12 different positions of high symmetry to find the most stable adsorption position shown in Figure 1,

and the most stable adsorption was observed in the H3 position. We calculated the adsorption of hydrogen molecules on COF-1 for reference; the adsorption energy is  $-0.048$  eV, which indicates that the interaction between the hydrogen molecules and the COF-1 layer is very weak. Figure 1b shows the calculated band structure. The original single-layer COF-1 showed semiconductor behavior, and we observed a band gap of 3.71 eV using the PBE method, consistent with a previous study.<sup>59</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Single Sc Atom-Decorated COF-1.** First, we investigated the adsorption of a single Sc atom on the COF-1 cell structure. Figure 2a shows the optimized geometry of the structure. We tested the adsorption of Sc atoms in 12 highly symmetrical positions and found that it will always move to the H3 position after the fully optimized geometry. The results show that Sc atoms prefer to be adsorbed at the H3 position of COF-1, and their binding energy is  $-2.708$  eV. From the Mulliken population, it is found that the Sc atom approaching the COF-1 sheet has a positive charge of  $1.44e$ , while all of the carbon atoms on the C ring around the Sc atom have a



**Figure 4.** Optimized atomic structures of Sc-COF-1 with adsorption of (a) one H<sub>2</sub>, (b) two H<sub>2</sub>, (c) three H<sub>2</sub>, (d) four H<sub>2</sub>, and (e) five H<sub>2</sub> molecules.

negative charge. Therefore, the difference in the potential of the electron causes an electric field to be generated between the positively charged Sc atoms and the negatively charged C atoms, resulting in an enhanced interaction between Sc and COF-1. Furthermore, the density of states (DOS) of the C six-membered ring near the Sc atom and the Sc atom was calculated to study the interplay between the Sc atom and the COF-1 cell layer, as shown in Figure 2b. There is a large peak overlap between the d orbital of Sc and the p orbital of C close to Fermi energy ( $E_F$ ) that indicates a powerful hybridization between the COF-1 structure and Sc atom. Therefore, the Sc atoms can be stably adsorbed on COF-1. Due to the strong s-p and p-p hybridization between the Sc atoms and the COF-1 layer, Sc has excellent stability on the COF-1 layer without agglomeration. This ensures that each Sc atom can maximize the adsorption of hydrogen molecules in the subsequent hydrogen storage research. The transfer of electrons from Sc to COF-1 causes the band gap to decrease, as shown in Figure 2c, which can also be observed in the C<sub>2</sub>N<sup>60</sup> complex and  $\gamma$ -graphyne.<sup>61</sup>

When another Sc atom is adsorbed on the Sc-COF-1 structure, the adsorption energies in two cases are calculated and compared, namely, two Sc atoms being on opposite sides and two Sc atoms being on the same side of COF-1, as shown in Figure 3a,b. It is found that the average adsorption energy (−3.252 eV) of the two Sc atoms on the opposite sides of COF-1 is lower than that of the two Sc atoms on the same side of COF-1 (−3.173 eV). This means that two Sc atoms tend to be adsorbed symmetrically on COF-1, which is consistent with previous studies.<sup>56,62,63</sup> Subsequently, we studied the maximum concentration coverage of Sc atoms on COF-1. The results show that up to six Sc atoms can be firmly adsorbed on COF-1 (6Sc-COF-1) sites on both sides, with an average binding energy of −3.23 eV, as shown in Figure 3c.

**3.2. Adsorption of H<sub>2</sub> Molecules on Sc-COF-1.** Figure 4a–d shows the optimized geometry structure of H<sub>2</sub> molecules adsorbed on the structure of Sc-COF-1 one by one. In Figure 4a, one H<sub>2</sub> molecule is adsorbed on the Sc-COF-1 structure, which greatly affects the COF-1 layer and the adsorption site of the Sc atom. It is observed that the COF-1 layer is obviously distorted. The Sc atom moves from the center to one side of the C six-membered ring, and the H<sub>2</sub> molecule is located above the other side of the C six-membered ring. When another H<sub>2</sub> molecule is adsorbed, two H<sub>2</sub> molecules are adsorbed on both

sides of the Sc atom and are symmetric about the Sc atom. Interestingly, the deformation degree of the COF-1 layer has been weakened, as shown in Figure 4b. Also, the deviation of the Sc atom from the benzene ring center is corrected, which is located again above the benzene ring center. In Figure 4c, when the structure adsorbs the third H<sub>2</sub> molecule, the deformation of the COF-1 layer is further corrected, in which the three H<sub>2</sub> molecules are in the same plane. The Sc atom is located directly over the benzene ring. When the fourth H<sub>2</sub> molecule is adsorbed on the Sc-COF-1 system, the four hydrogen molecules exhibit a symmetrical and tilted distribution around the Sc atoms. Moreover, the COF-1 layer and the Sc atom both revert to their original configuration, as displayed in Figure 4d. The continuous adsorption energy and the average adsorption energy of hydrogen molecules are shown in Table 1. It can be seen that the continuous

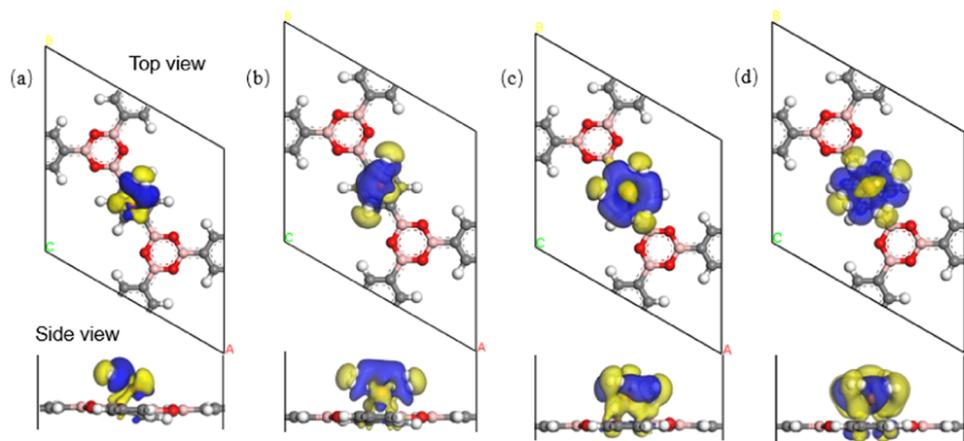
**Table 1.** Average Adsorption Energy  $\bar{E}_{ad}$  and Continuous Adsorption Energy  $E_{ad}$  of H<sub>2</sub> Molecules on the Single Side Sc-Decorated COF-1<sup>a</sup>

number of H <sub>2</sub>	1	2	3	4	5
$\bar{E}_{ad}$ (eV)	−0.51	−0.49	−0.41	−0.28	−0.11
$E_{ad}$ (eV)	−0.51	−0.50	−0.47	−0.42	
$d_H$ (Å)	0.803	0.796	0.805	0.821	0.815

<sup>a</sup> $d_H$  (Å) is the average bond length of  $nH_2$  molecules.

adsorption energy and the average adsorption energy of hydrogen molecules are increased as the number of H<sub>2</sub> molecules adsorbed increases. When the fifth H<sub>2</sub> molecule is adsorbed, its continuous adsorption energy is only −0.116 eV, which goes beyond the satisfactory adsorption value of H<sub>2</sub> molecules from −0.2 to −0.7 eV.<sup>41</sup> The fifth H<sub>2</sub> molecule can be adsorbed at 0 K due to its negative adsorption energy; however, it is still not suitable for practical application because it may not be adsorbed at room temperature. Therefore, considering the practical application, it is considered that up to four H<sub>2</sub> molecules can be stably adsorbed around the Sc atom.

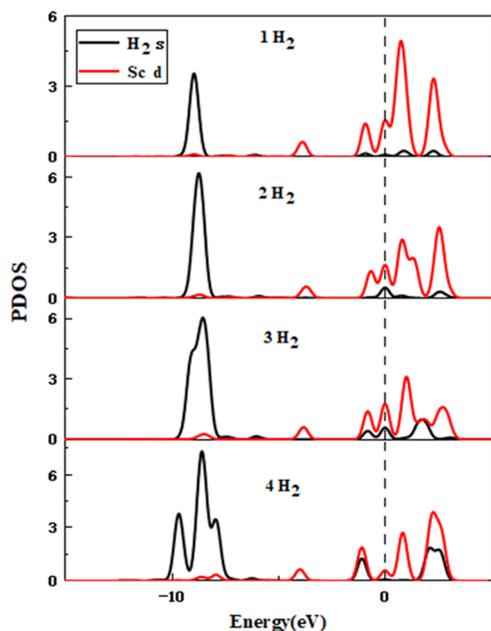
To study the interplay between H<sub>2</sub> and the Sc-COF-1 structure, the charge density differences of Sc-COF-1 adsorbed by 1H<sub>2</sub>–4H<sub>2</sub> molecules have been calculated as shown in Figure 5. It is easy to see that the charge accumulation (blue areas) occurs mainly between H<sub>2</sub> molecules and Sc atoms, which indicates that there is a strong interaction between them.



**Figure 5.** Electronic charge density differences for different numbers of H<sub>2</sub> adsorbed on Sc-COF-1: adsorption of (a) one H<sub>2</sub>, (b) two H<sub>2</sub>, (c) three H<sub>2</sub>, and (d) four H<sub>2</sub> molecules. The isosurface is 0.008 e/Å<sup>3</sup>.

The charge is accumulated on the side of H<sub>2</sub> molecules closer to the Sc atom, which corresponds to the  $\sigma$  orbital of H<sub>2</sub> molecules, while the side far away from the Sc atom loses charge, which corresponds to the  $\sigma^*$  orbital of H<sub>2</sub> molecules. The Mulliken population analysis shows that the charges of the two hydrogen atoms in the H<sub>2</sub> molecule are  $-0.12e$  and  $-0.10e$ , respectively. This indicates that the H<sub>2</sub> molecule gets the charges from the positively charged Sc atom and is polarized.

We have calculated the partial density of states (PDOS) for the adsorption of 1–4 H<sub>2</sub> adsorbed by Sc-COF-1 to further investigate the mechanism of the adsorption of H<sub>2</sub> on Sc-COF-1, and the results are shown in Figure 6. It can be observed that the main peaks of the H<sub>2</sub> molecules are all around  $-9$  eV, which corresponds to the  $\sigma$  orbitals of the H<sub>2</sub> molecules.<sup>56,63</sup> The 1s orbital of the H<sub>2</sub> molecule and the 3d orbital of Sc overlap slightly at  $-9$  eV. Also, the orbitals are overlapped obviously near Fermi energy, which means that the electrons

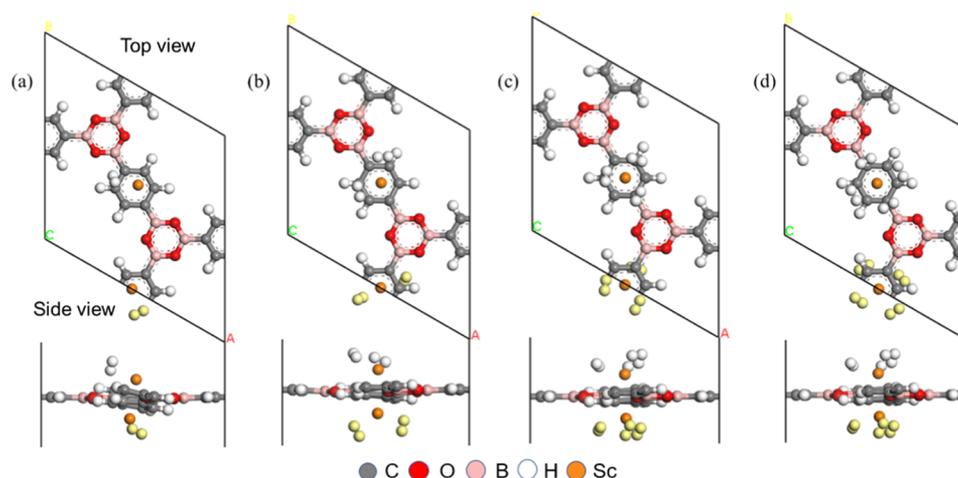


**Figure 6.** PDOS of Sc d and H<sub>2</sub> s orbitals for one to four H<sub>2</sub> adsorbed on the Sc-COF-1 cell layer.

filling the Sc 3d orbital are fed back to the  $\sigma^*$  orbitals of H<sub>2</sub>. From this result, it is seen that the Kubas back-donation effect<sup>41,64–66</sup> plays an important role in the adsorption of H<sub>2</sub> molecules on the Sc atom. By comparing these PDOS, it is found that there is a band broadened around  $-9$  eV with the increase of H<sub>2</sub> adsorbed. It is considered that this phenomenon results from the interaction between H<sub>2</sub> molecules. In addition, as the number of H<sub>2</sub> molecules adsorbed on Sc-COF-1 increases, the  $\sigma$  orbital of the H<sub>2</sub> molecule shifts to the right. This shows that the interaction between the H<sub>2</sub> molecule and Sc-COF-1 gradually weakens. The peak of the  $\sigma$  orbital of the H<sub>2</sub> molecule splits into several peaks after the fourth H<sub>2</sub> molecule is adsorbed, which means that there is a very weak interplay between H<sub>2</sub> and the Sc atom. This conclusion is consistent with Table 1.

For the case of COF-1 modified by two Sc atoms on both sides (2Sc-COF-1), the hydrogen storage performance has also been explored. Figure 7a presents this structure model, which is similar to Sc-COF-1. The Sc atom is deviated from the center of the C six-membered ring, and the COF-1 structure is deformed to a certain extent when the first H<sub>2</sub> is adsorbed around the Sc atom. However, when the second H<sub>2</sub> atom is adsorbed, the Sc atom returns to the center of the C six-membered ring, and the deformation of the COF-1 structure is also repaired to a certain extent, as displayed in Figure 7b. The relevant adsorption energy is shown in Table 2, in which it can be seen that four hydrogen molecules could be adsorbed stably on every Sc atom. Similar to the adsorption of H<sub>2</sub> molecules on Sc-COF-1, the more H<sub>2</sub> are adsorbed on 2Sc-COF-1, the lower the adsorption energy.

We found that the Sc atoms do not show aggregation from the optimized geometry structure of 6Sc-COF-1 because the Coulomb force between Sc atoms repels each other and the strong interplay between Sc and COF-1. In addition, the large distance between Sc atoms makes it difficult to generate aggregation. Research shows that up to six Sc atoms can be stably adsorbed on COF-1, namely, 6Sc-COF-1. Thus, the 6Sc-COF-1 structure can adsorb up to 24 H<sub>2</sub> molecules. The relaxed structures are shown in Figure 8d. Figure 8a,b shows that the H<sub>2</sub> molecule is adsorbed on each Sc atom one by one. The COF-1 layer undergoes significant deformation, and when the second H<sub>2</sub> molecule is adsorbed on each Sc atom, the deformation has been partially repaired. The 6Sc-COF-1 structure is further repaired with another H<sub>2</sub> molecule being



**Figure 7.** Optimized geometry of 2Sc-COF-1 with adsorption of (a) one H<sub>2</sub>, (b) two H<sub>2</sub>, (c) three H<sub>2</sub>, and (d) four H<sub>2</sub> molecules per Sc atom.

**Table 2.** Average Adsorption Energy  $\bar{E}_{ad}$  and Continuous Adsorption Energy  $E_{ad}$  of H<sub>2</sub> on 2Sc-COF-1

number of H <sub>2</sub>	2	4	6	8
$\bar{E}_{ad}$ (eV)	-0.516	-0.483	-0.472	-0.276
$E_{ad}$ (eV)	-0.516	-0.499	-0.490	-0.437

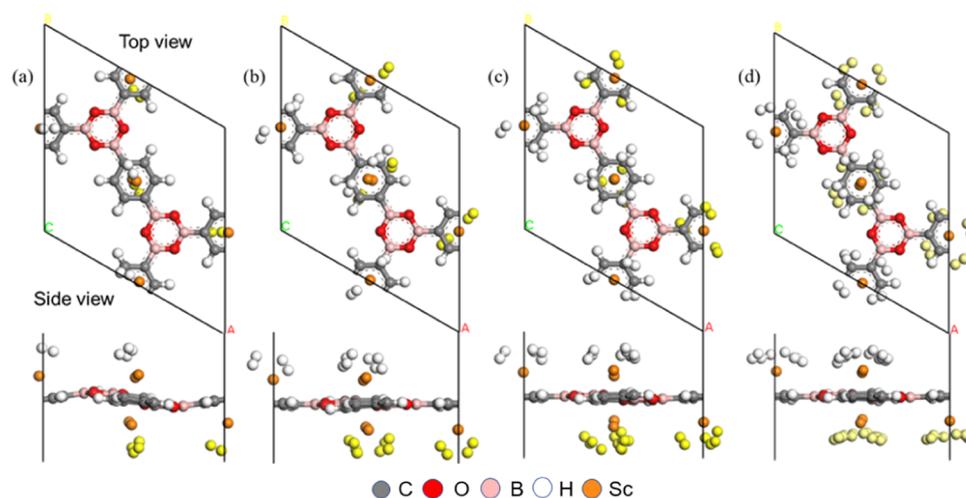
**Table 3.** Average Adsorption Energy  $\bar{E}_{ad}$  and Continuous Adsorption Energy  $E_{ad}$  of H<sub>2</sub> Molecules on 6Sc-COF-1

number of H <sub>2</sub>	6	12	18	24
$\bar{E}_{ad}$ (eV)	-0.445	-0.362	-0.255	-0.215
$E_{ad}$ (eV)	-0.445	-0.403	-0.354	-0.319

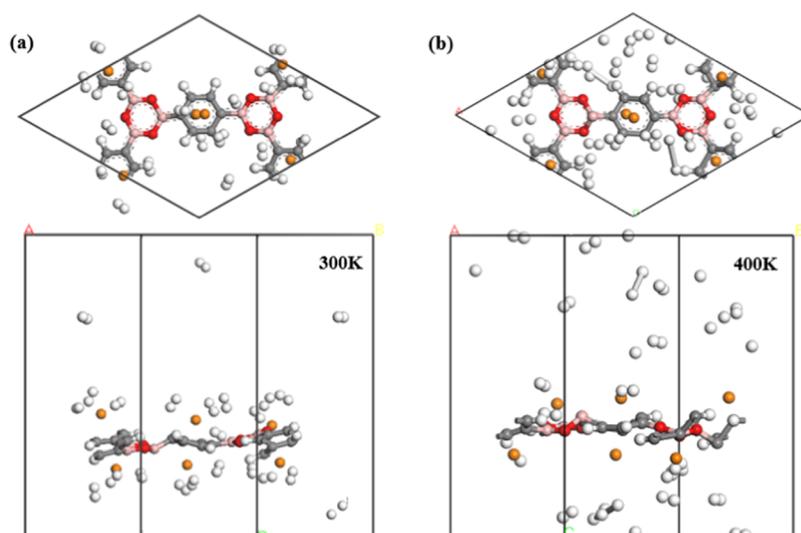
adsorbed on each Sc atom (as seen in Figure 8c). For the 6Sc-COF-1 structure, every Sc atom also can stably adsorb four H<sub>2</sub> molecules. Thus, 24 H<sub>2</sub> molecules in total can be adsorbed. In this case, the 6Sc-COF-1 layer is restored to its original configuration. The corresponding average adsorption energy  $\bar{E}_{ad}$  and the adsorption energy  $E_{ad}$  are shown in Table 3. It can be seen that the average energy  $\bar{E}_{ad}$  and the adsorption energy  $E_{ad}$  are both in a reasonable range of 0.2–0.4 eV.<sup>67</sup> The hydrogen adsorption capacity reaches 6.78 wt %, which implies that Sc-decorated COF-1 is a promising hydrogen adsorption material.

Finally, we used ab initio molecular dynamics (MD) in the CASTEP simulation to simulate the hydrogen desorption behavior of the Sc-modified COF-1 surface. The parameters are set to a constant number of atoms, a constant volume, and constant temperatures of 300 and 400 K. We set the MD

simulation time to 1.5 ps to have enough time to complete the calculation, which is consistent with the published reports.<sup>56,63,68–70</sup> Figure 9a,b shows the molecular dynamics simulation results of the adsorption of 24 H<sub>2</sub> molecules by 6Sc-COF-1 at 300 and 400 K, respectively. It can be seen that the COF-1 structure does not undergo significant deformation and the six Sc atoms are still stably adsorbed on the COF-1 layer without aggregation at both 300 and 400 K. One of the four hydrogen molecules adsorbed by each Sc atom escapes at 300 K, and all of the adsorbed H<sub>2</sub> molecules are released when the temperature is 400 K. It is demonstrated that the adsorption and desorption of hydrogen molecules can be achieved within a narrow temperature range of 300–400 K and 6Sc-COF-1 has excellent reversibility as a hydrogen storage material. Also, the hydrogen adsorption capacity at environmental temperature is 5.23 wt %, which is higher than the DOE standard (4.5 wt %).



**Figure 8.** Optimized geometry structure of 6Sc-COF-1 with adsorption of (a) one H<sub>2</sub>, (b) two H<sub>2</sub>, (c) three H<sub>2</sub>, and (d) four H<sub>2</sub> molecules per Sc atom.



**Figure 9.** Snapshots of the 6Sc-COF-1-24 H<sub>2</sub> model after 1.5 ps molecular dynamics simulations at (a) 300 K and (b) 400 K.

#### 4. CONCLUSIONS

To summarize, we studied the hydrogen adsorption capability of Sc-decorated COF-1 based on DFT theory. The results show that six Sc atoms can be stably adsorbed on the COF-1 layer and each Sc atom can adsorb four H<sub>2</sub> molecules. Thus, the hydrogen storage capacity of the 6Sc-COF-1 system reaches 6.78 wt %. The ab initio MD simulation results show that 18 H<sub>2</sub> molecules can be adsorbed stably on the 6Sc-COF-1 layer with a hydrogen adsorption capacity of 5.23 wt % at 300 K, which is higher than that of the DOE standard (4.5 wt %). Also, the hydrogen molecules adsorbed on the 6Sc-COF-1 layer are all dissociated at 400 K. Therefore, the COF-1 layer modified by Sc atoms is expected to be a promising reversible hydrogen storage medium at room temperature.

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##### Notes

The authors declare no competing financial interest.

The raw data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

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