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RESEARCH ARTICLE

Tripyrrylmethane based 2D porous structure for hydrogen storage

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The key to hydrogen storage is to design new materials with light mass, large surface and rich adsorption sites. Based on the recent experimental success in synthesizing tripyrrylmethane, we have explored Ti-tripyrrylmethane based 2D porous structure for hydrogen storage using density functional theory. We have found that the structure is stable, and the exposed Ti sites can bind three hydrogen molecules with an average binding energy of 0.175 eV/H_2, which lies in the energy window for storage and release of hydrogen in room temperature and at the ambient pressure.

Keywords tripyrrylmethane, hydrogen storage

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Hydrogen, as a clean, renewable and efficient energy carrier, has been attracting tremendous attentions in recent years. One of the current main obstacles of hydrogen economy is its efficient storage, which should have high gravimetric and volumetric density, and fast kinetics [1–3]. The US Department of Energy (DOE) has set the 6 wt% gravimetric density target for H_2 storage near room temperature and under ambient pressure. Many solid materials have been investigated as hydrogen storage mediums, including metallic hydrides, complex hydrides, nanostructures, and metal-organic frameworks (MOFs) [4–7]. However, no existing materials meet all the industry requirements. Conventionally, the interactions between hydrogen and host substrate materials are either too weak as in physical adsorption or too strong as in chemical absorption. Therefore, new materials need to be designed with the following basic requirement: light materials with large available surface areas and with rich effective absorption sites. The widely studied MOFs have large surfaces, but the adsorptive sites are not effective, where metal atoms are coordinated with oxygen/nitrogen containing ligand groups to form a metal-oxygen/nitrogen octahedron or tetrahedron, which are connected through sharing edges. In such systems, metal atoms in the frameworks are on the cross connecting points, hardly being exposed to absorb hydrogen molecules, so they can only be used for hydrogen storage in low temperature under high pressure. To improve hydrogen storage performance, we need to design a porous material with rich unsaturated metal sites. In order to prevent metal sites from clustering [8], the interaction with the substrate should be stronger than that with metal itself. In this study, based on the above principles together with the recent experimental findings, we theoretically explored Ti-tripyrrylmethane based 2D porous structure with isolated and exposed metal sites for hydrogen storage.

Systematic calculations were carried out using density functional theory (DFT) with the generalized gradient approximation (GGA) with spin polarization. Exchange correlation based on Perdew–Wang (PW91) [9] form was used as implemented in DMol3 [10, 11]. Vacuum space of 10 Å along z direction for 2D framework was applied to avoid interaction with images. Monkhorst–Pack special k point [12] of 3×3×1 meshes are used to represent the Brillouin zone for 2D polymer structure. We used effective core potential with double numerical polarized (DNP) basis set. The orbital cutoff is set global with the value of 5.2 Å. All structures were optimized without symmetry constraints. The convergence criteria for energy, force and maximum displacement are set to be 10^{-6} Ha, 1×10^{-3} Ha/Å and 0.005 Å, respectively. The binding energy per H_2 adsorbed on substrate can be calculated from equation $E_\mathrm{b} = (nE_{\mathrm{H}_2} + E_\mathrm{substrate} - E_{n\mathrm{H}_2-\mathrm{substrate}})/n$. The accuracy of our computational method was tested by computing the binding energy and bond length of H_2. The calculated bond length and binding energy of H_2 are 0.748 Å and 4.59 eV, respectively, which are in good agreement with the experimental values of 0.741 Å and 4.533 eV [13]. Our discussions below will start with a structural unit and then dimers and finally extend to a 2D structure.

We use tripyrrylmethane (TPM) as a structural unit, which has been synthesized in a recent experiment [14]. The TPM complex consists of three pyrrole molecules (C_4NH_5) linked together by one sp^3 hybridized C forming a propeller-like structure. As shown in Fig. 1(a), the bond length between the central C and any pyrrole is 1.516 Å. Now we remove the H atoms at N sites and introduce a Ti atom. Optimization indicates that Ti absorption causes structural deformation and three Ti–N bonds are formed, resulting in a highly symmetric structure with the symmetry of C_{3v}, and the dihedral angel between any two pyrrole molecules is 120°. Figure 1(b) and (c) show the side view and top view of the geometry, labeled as Ti–TPM. From TPM to Ti–TPM (TPM + Ti → Ti–TPM $+1.5H_2$), the binding energy ΔE ($= E_{\text{Ti–TPM}} + 1.5E_{H_2} - E_{\text{TPM}} - E_{\text{Ti}}$) is found to be –3.113 eV. In Ti–TPM, Ti is three-fold coordinated with only N sites, being exposed for adsorption, which can be further verified by checking the lowest unoccupied molecular orbital (LUMO), as plotted in Fig. 1(d). We can clearly see that the main components are from Ti unfilled d_z^2 orbita, so Kubas interaction [15] will happen when hydrogen molecules are introduced. In addition, owing to the difference in electronegativity between Ti and N, Ti atom is positively charged with the charge of +0.675 electron, and the produced local electric field from the positively charged Ti ion can further polarize H_2 molecules, causing electrostatic attractions [16]. We have found that Ti site can adsorb three H_2 molecules (Fig. 2) with the average binding energy per H_2 of 0.172 eV, which lies in the required ideal hydrogen storage binding range [17], namely, 0.1 ∼ 0.2 eV/H_2. The average distance of Ti–H is found to be 2.26 Å, and the H–H bond length is elongated to 0.764 Å from its free state (0.741 Å). Due to the steric hindrance of the vicinal hydrogen atoms in the pyrrole rings, we could not add more H_2 molecules to Ti site.

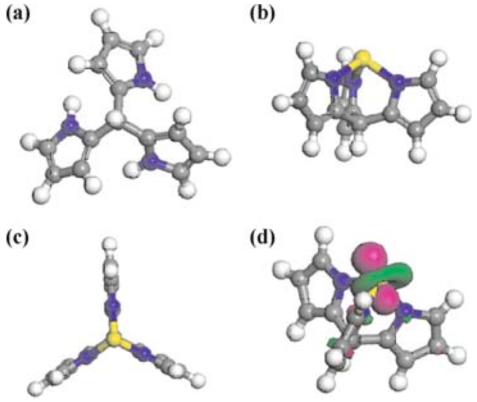

Fig. 1 Geometry of TPM **(a)**, side view **(b)** and top view **(c)** of Ti-TPM, the LUMO of Ti–TPM **(d)**. Gray, blue, yellow and white balls represent C, N, Ti, and H.

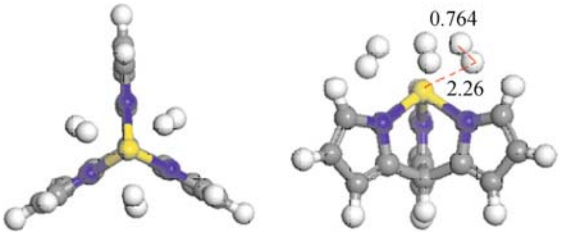

Fig. 2 Geometry of di–TPM absorbing $3H_2$ with top view and side view.

Next, we use Ti–TPM as a building block to construct a dimer through C–C bonding, labeled as di–TPM. There are two possible configurations (Fig. 3): dimer I (connected through the C neighboring to N site), and dimer II (connected through the meta-position). Our calculations suggest that the reactions: TPM +TPM → di–TPM (dimer I or II) + H_2 are endothermic with the formation energies of 0.388 and 0.604 eV for dimer I and dimer II, respectively. This indicates that the two reactions require energy to take place. It is important to

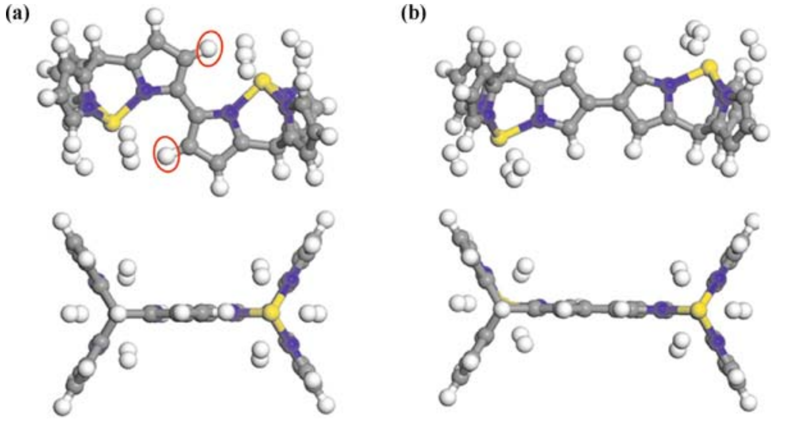

Fig. 3 H_2 molecules adsorbed in dimers in their side view (up panel) and top view (down panel) for dimer I **(a)** and dimer II **(b)** configurations. The red circles show the H atom causing the steric hindrance.

note that a similar dimerization reaction has been successfully carried out experimentally [18]. Geometric optimizations show that in both dimers the linked two pyrroles are located in the same plane and the structures are stiff and stable. Similarly, we introduce six H_2 molecules to both of the two dimers, and each Ti atom can again adsorb three H_2 molecules. The average binding energies of H_2 molecules are found to be 0.131 eV/H_2 and 0.177 eV/H_2 with the average Ti–H distance of 2.28 and 2.25 Å for dimer I and dimer II respectively. The reasons for the different behaviors between dimer I and dimer II are as follow: in dimer I the four inboard H_2 are away from the original position compared to the monomer structure, which is due to the steric hindrance caused by the H atoms in the pyrrole rings as shown in the red circles in Fig. 3(a). However, the dimer II does not have such a problem and the H_2 adsorption behaves similarly as that in the monomer situation.

The desirable adsorption of H_2 molecules in Ti–TPM dimers encourages us to extend to large structures through polymerization. As far as we know, no such polymerization reactions have been successfully achieved so far. However, note that the two linked pyrroles in di–TPM are located in the same plane, and the three pyrroles in each TPM have dihedral angles of 120°, then it is possible to assemble these di–TPMs molecules into polymerized structure via chemical reaction in appropriate condition. In view of the better performance of dimer II, we use it to build a 2D porous framework [Fig. 4(a)] where the rhombus unit cell contains one di–TPM dimer II. The formation from dimer II to a 2D structure is found to be endothermic with the formation energy of 1.067 eV/unit cell. And this poly-Ti–TPM framework is a novel porous structure with unsaturated Ti exposed near its linking site. The geometric optimization shows that the distance between the two nearest neighbor pore centers is 15.30 Å, which is also the unit cell lattice. We plotted the wave function of lowest unoccupied (LU) state [Fig. 4(b)], which is highly located at Ti sites, similar to its monomer case. This demonstrates that H_2 molecules can again be adsorbed. When three H_2 molecules are introduced to each Ti site in the optimized poly-Ti–TPM framework structure (Fig. 5), the average binding energy of H_2 molecules is found to be 0.175 eV/H_2, suggesting that hydrogen delivery can be operated under the ambient environment. The gravimetric density is 2.3 wt%. Although this value is lower than the target of H_2 storage set by DOE, it is still higher than any existing MOFs in the same condition. This 2D porous structure suggests a possible way to introduce exposed unsaturated metal sites in the framework serving as reactive site to adsorb H_2 through Kubas mechanism and polarization. And we anticipate that owing to large pores of this poly-Ti–TPM structure and the unbalanced charge distribution in the system, more H_2 molecules can be stored through van der Waals and electrostatic interaction. Due to the limitation of DFT, we could not include the contribution from these weak interactions in

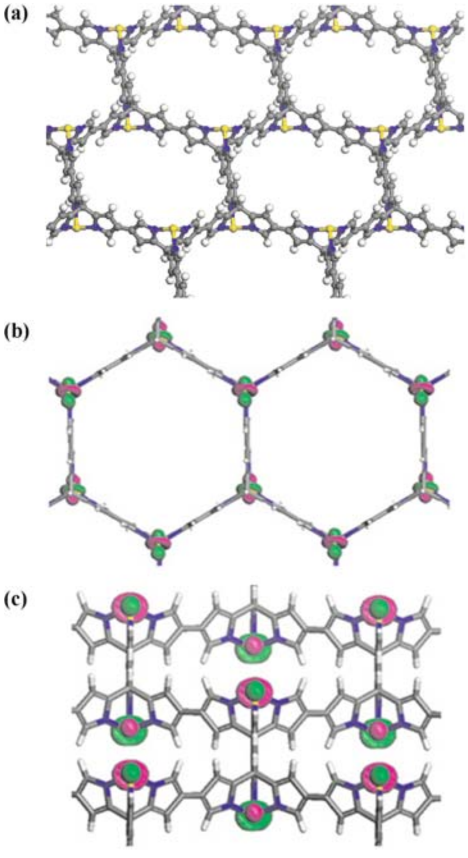

Fig. 4 Geometry **(a)** and wave function isosurface of LU state in top view **(b)** and side view **(c)** of 2D poly-Ti–TPM.

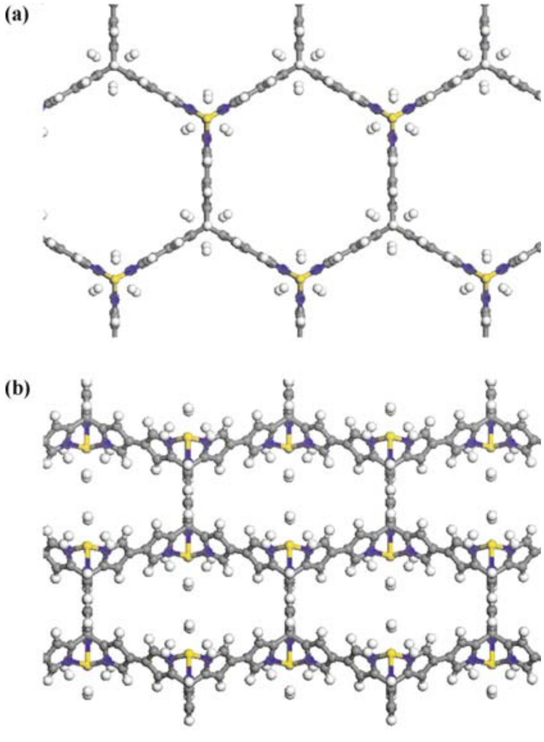

Fig. 5 Hydrogen adsorption in 2D poly-Ti–TPM with top view **(a)** and side view **(b)**.

our present calculations. Further studies for this system using Monte Carlo simulation are underway.

In summary, based on the recent experimental findings in synthesis of TPM and its dimerization, we explored a novel 2D porous structure with exposed unsaturated Ti sites for hydrogen storage. The following conclusions have been drawn: 1) Energetics study shows that the insertion of Ti into TPM is exothermic, the polymerization for Ti–TPM to a dimer and a 2D structure is endothermic; 2) 2D poly-Ti–TPM structure is a stable porous framework with a pore size of 15.30 Å; 3) Each Ti site can adsorb three H_2 molecules. Electronic structure shows that the lowest unoccupied orbital is contributed mainly from Ti-3d orbital, and the resulting Kubas interaction together with polarization give the average binding energy of 0.172 eV/H_2, which lies in the ideal energy window for operating storage and release in room temperature and under ambient pressure; 4) The corresponding gravimetric density of H_2 stored on the 2D porous TPM material is 2.3 wt%, higher than any existing MOFs in the same condition. The present study suggests that metal-organic super molecular hybrid porous structure is promising for hydrogen storage. We hope that this paper will stimulate further experimental effort in this direction.

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