# SUPPLEMENTARY INFORMATION

# DFT Insight into Comparative Hydrogen Adsorption and Hydrogen Spillover Mechanisms of $Pt_4$/graphene and $Pt_4$/anatase (101) Surfaces

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**1. $Pt_4$ cluster**

Three common isomers (parallelogram, tetrahedral and square planer) of $Pt_4$ cluster were optimized to find the most stable configurations (Figure S1). Table S1 shows that the cohesive energies among those three isomers are isoenergetic with Pt-Pt bond length 2.58 Å. Cohesive energy was calculated using the formula:

$E_{coh} = E(Pt_4) - 4E(Pt)$

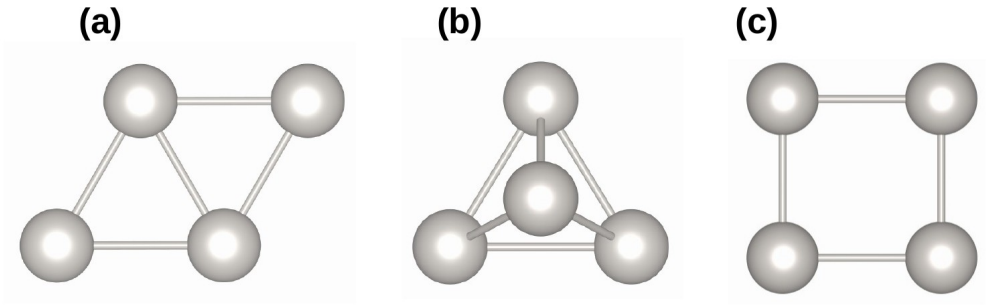


**Figure S1**: Different isomers of $Pt_4$ cluster: (a) parallelogram; (b) tetrahedral; (c) square planer.

**Table S1**: Cohesive energies, $E_{coh}$ (eV) and average bond lengths, d(Pt-Pt) (Å) bond length for three different isomers of $Pt_4$ cluster.

| $Pt_4$ Isomer | $E_{coh}$ (eV) | d(Pt-Pt) (Å) |
|---|---|---|
| Tetrahedral | -2.79 | 2.58 |
| Parallelogram | -2.77 | 2.51 |
| Square | -2.76 | 2.44 |

## 2. $Pt_4$ binding to graphene and anatase (101) surfaces

3D tetrahedral $Pt_4$ adsorption on three different sites of graphene and one site of anatase (101) are shown in Figures S2 and S3 respectively. Their orbital-decomposed DOS of $Pt_4$ adsorbed on both supports and the corresponding total DOS are depicted in Figures S4 and S5.

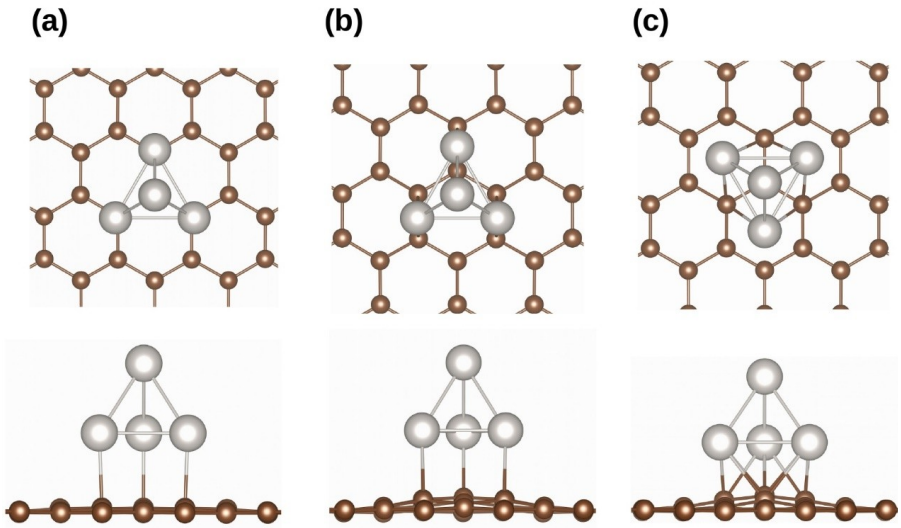


**Figure S2**: Optimized structures of $Pt_4$/graphene where the bottom atoms of $Pt_4$ adsorbed on graphene at different adsorption sites: (a) top; (b) bridge; (c) hollow (Grey, Pt; Brown, C).

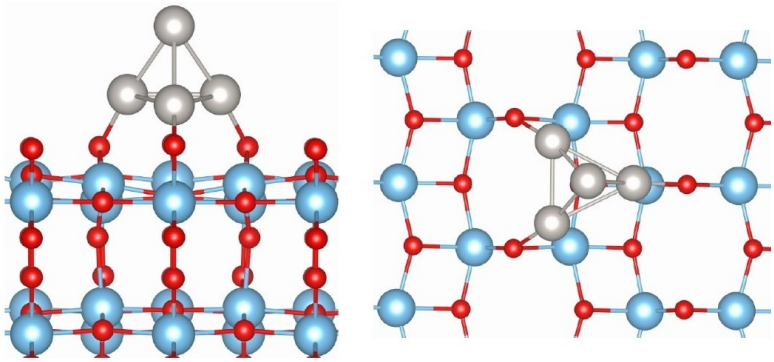

**Figure S3**: Optimized structures of $Pt_4$/anatase (101) where the bottom atoms of $Pt_4$ are adsorbed on 2-fold coordinated oxygen atoms ($O_{2c}$) of the anatase (101) surface (Grey, Pt; Blue, Ti; Red, O).

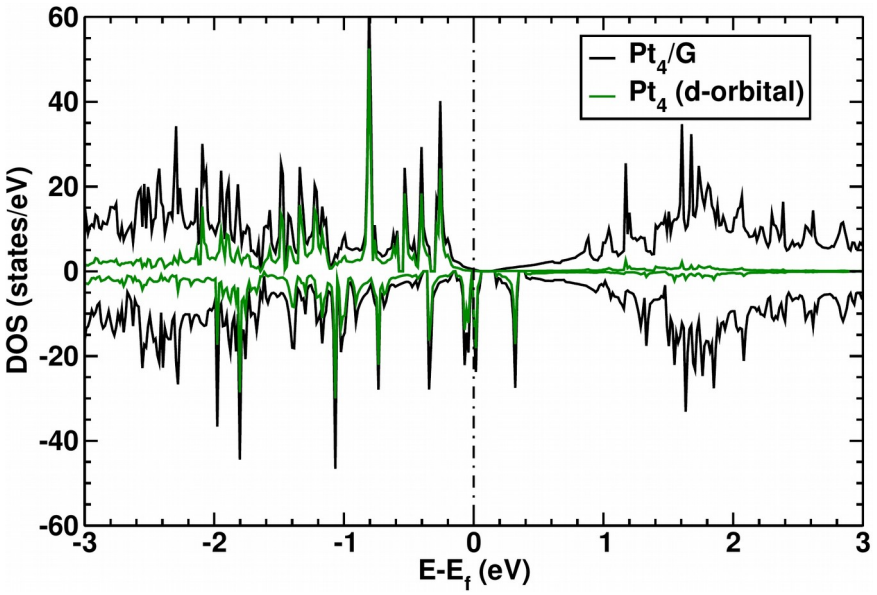


**Figure S4:** Orbital-decomposed DOS of $Pt_4$ adsorbed on graphene surface and total DOS of $Pt_4$/graphene (G stands for graphene).

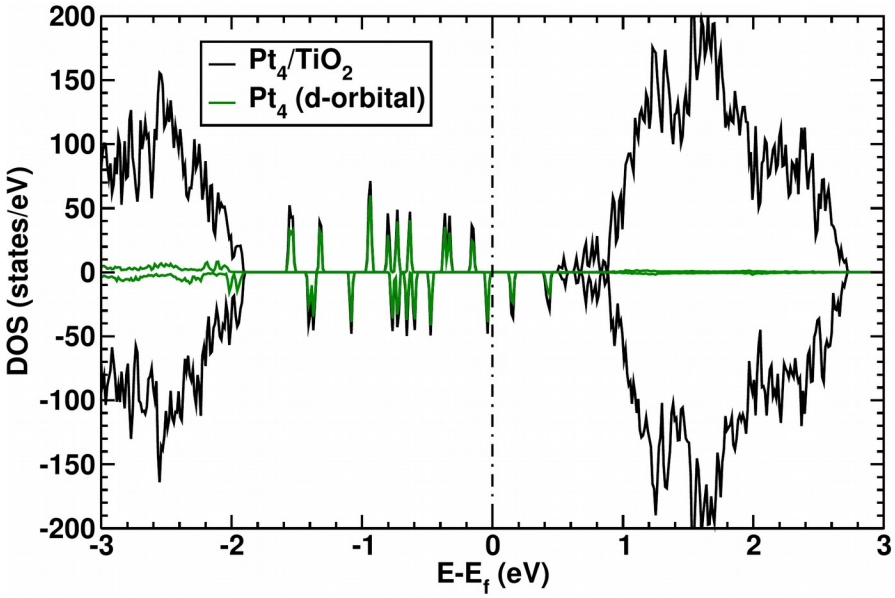


**Figure S5**: Orbital-decomposed DOS of $Pt_4$ adsorbed on anatase (101) surface and total DOS of $Pt_4/TiO_2$.

### 3. $H_2$ adsorption on bare graphene and anatase (101) surfaces

$H_2$ molecularly and dissociatively adsorption on bare graphene are illustrated in Figures S6(a) ~ S6(c) and S6(d) ~ S6(f) respectively. $H_2$ dissociatively adsorption on bare anatase (101) are showed in Figure S7.

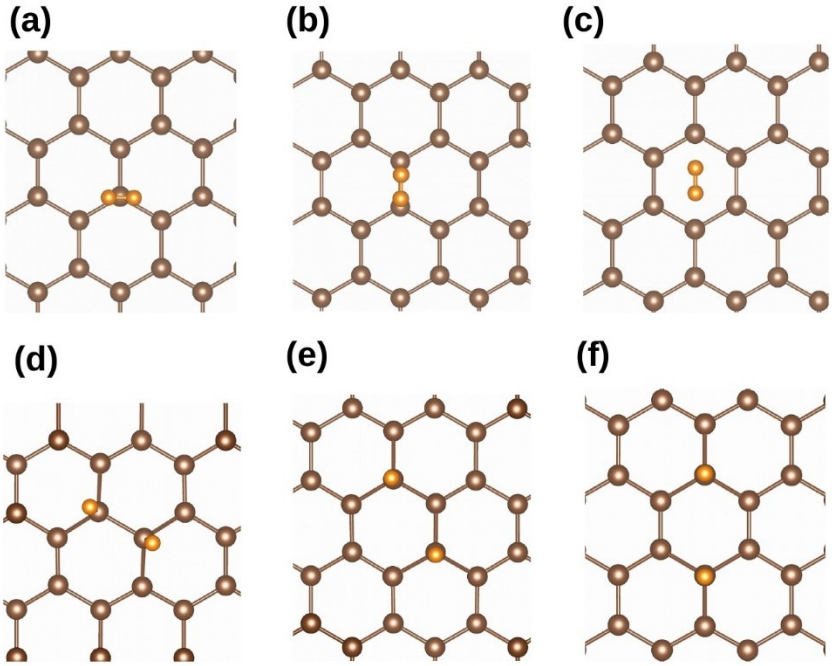


**Figure S6**: Optimized structures of $H_2$ molecularly adsorbed at (a) top, (b) bridge; (c) hollow sites, and dissociatively adsorbed at (d) ortho, (e) meta, (f) para C-top sites of graphene surface (Orange, H; Brown, C).

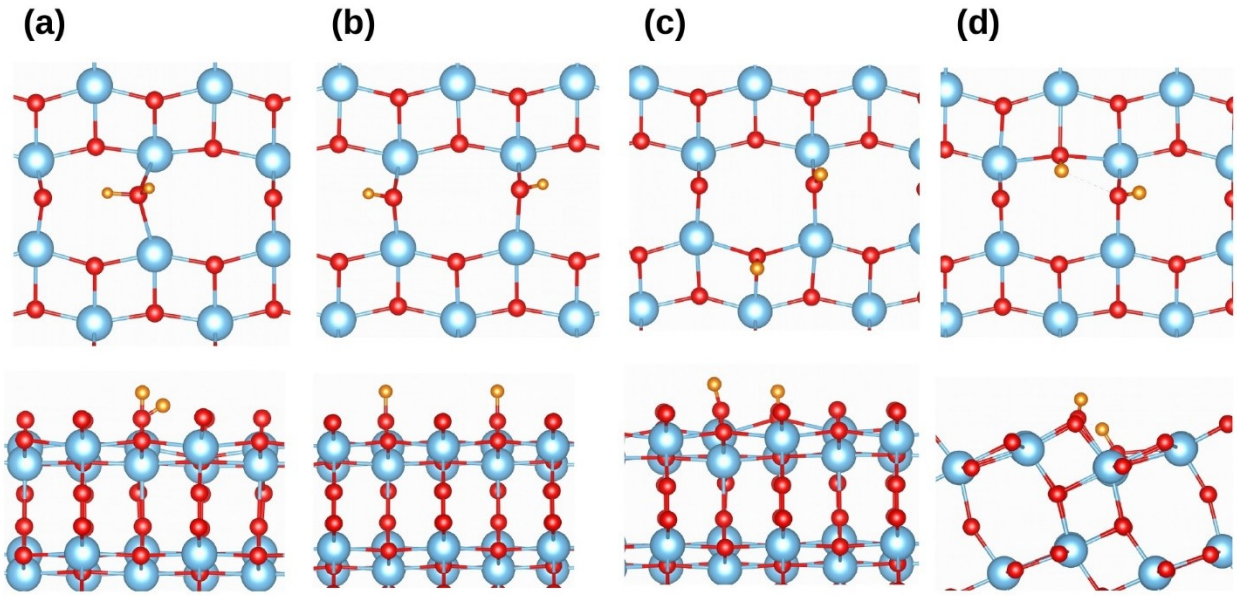


**Figure S7**: Optimized structures of $H_2$ dissociatively adsorbed at different sites: (a) $O_{2c}$; (b) $O_{2c}$-$O_{2c}$; (c) $O_{3c}$-$O_{2c}$; (d) $O_{3c}$-$O_{2c}$ of anatase (101) surface (Orange, H; Blue, Ti; Red, O).

When placing a $H_2$ molecule on a single 2-fold coordinated oxygen atom ($O_{2c}$) of anatase (101) surface leads to the formation of one $OH^-$ group and transfer two electrons to the nearby Ti atoms and thus reduces the oxide surface as can be seen from spin density plot where one unpaired electron is localized on nearest Ti atom and another unpaired electron is delocalized on Ti atoms of the subsurface (Figure S8a). When placing 2 H atoms on two different O atoms leads to two unpaired electrons localized on two Ti atoms (Figures S8b – S8d).

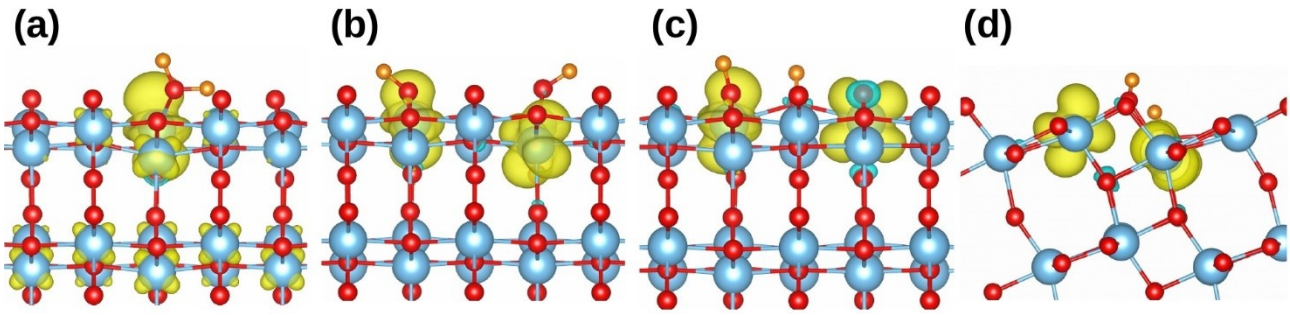


**Figure S8**: Spin density (in yellow) plots for $H_2$ dissociative adsorption on anatase (101) surface where unpaired electrons are (a) localized on one Ti and delocalized on subsurface Ti atoms; (b)~(d)localized on Ti atoms near H.

**4. Multiple H adsorption on a Pt atom and $Pt_4$ cluster**

The adsorption energies per H atom were calculated according to the following formula

$$E_{ads/H} = \{E(nHPt_m) – E(Pt_m) – n/2\ E(H_2)\}/n$$

Where m and n are number of Pt and H atoms respectively.

The comparative curves of H adsorption energy per H atom versus the number of H atom adsorbed on a Pt atom and a $Pt_4$ are illustrated in Figure S9. In these calculations, the maximum H numbers that a Pt and $Pt_4$ can uptake are 8 and 24 respectively, where their ratios of H:Pt are 8:1 and 6:1 for a Pt and $Pt_4$ with adsorption energies per H atom of -0.62 and -0.43 eV respectively.

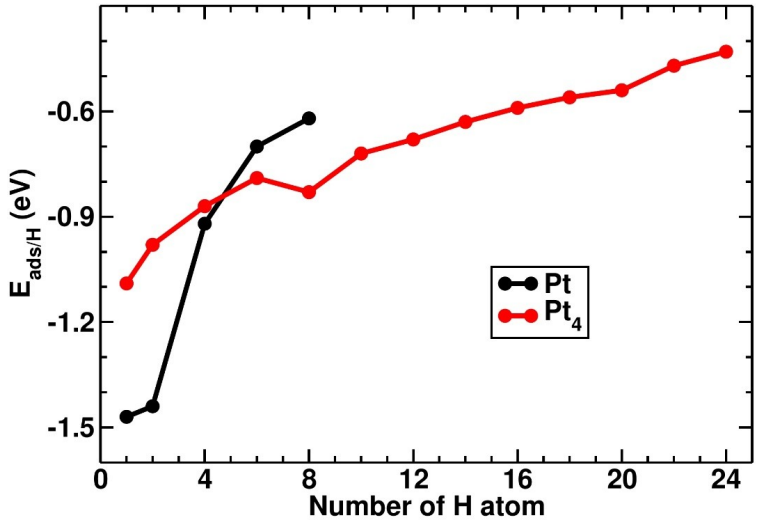


**Figure S9:** Adsorption energies per H atom of multiple $H_2$ dissociative adsorption on a single Pt atom and $Pt_4$ cluster.

## 5. $H_2$ adsorption on $Pt_4$/graphene and $Pt_4$/anatase (101) surfaces

$H_2$ molecularly physiosorbs on the most stable site (top of the C atom, Figure S10) of graphene in the presence of $Pt_4$ cluster with $E_{ads/H}$ of -0.20 eV. Differently, for anatase (101) surface, $H_2$ dissociatively chemisorbs on the most stable site (2-fold coordinated oxygen atom ($O_{2c}$), Figure S10) in presence of $Pt_4$ cluster with $E_{ads/H}$ of -0.35 eV.

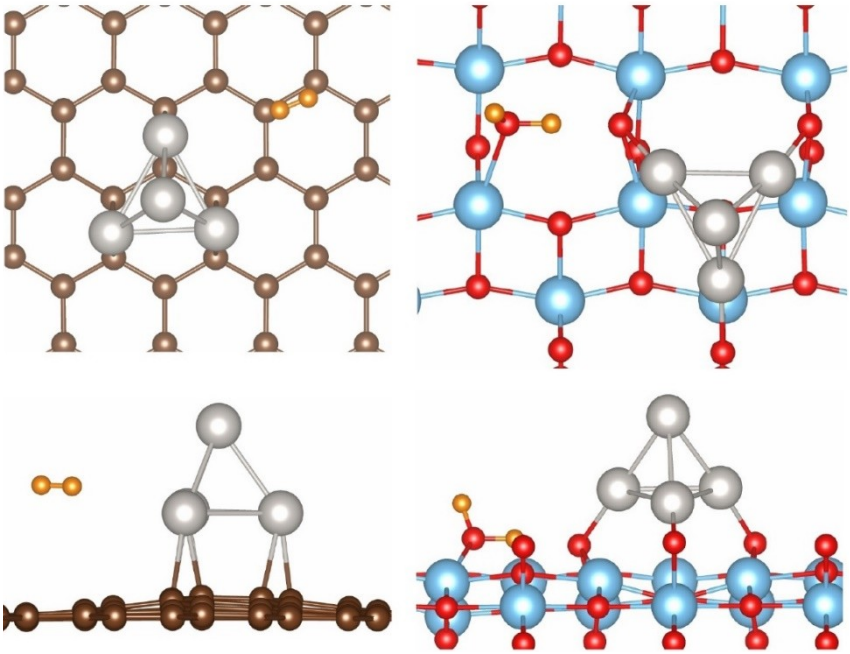

**Figure S10**: $H_2$ molecule adsorption on graphene and anatase (101) surfaces in presence of a $Pt_4$ cluster (Orange, H; Brown, C; Blue, Ti; Red, O; Grey, Pt).

## 6. One H atom adsorption on $Pt_4$ of $Pt_4$/graphene and $Pt_4$/anatase(101) surfaces

Atomic H adsorption on the $Pt_4$ surface of $Pt_4$/graphene and $Pt_4$/anatase(101) are shown in Figures 11 and 12.

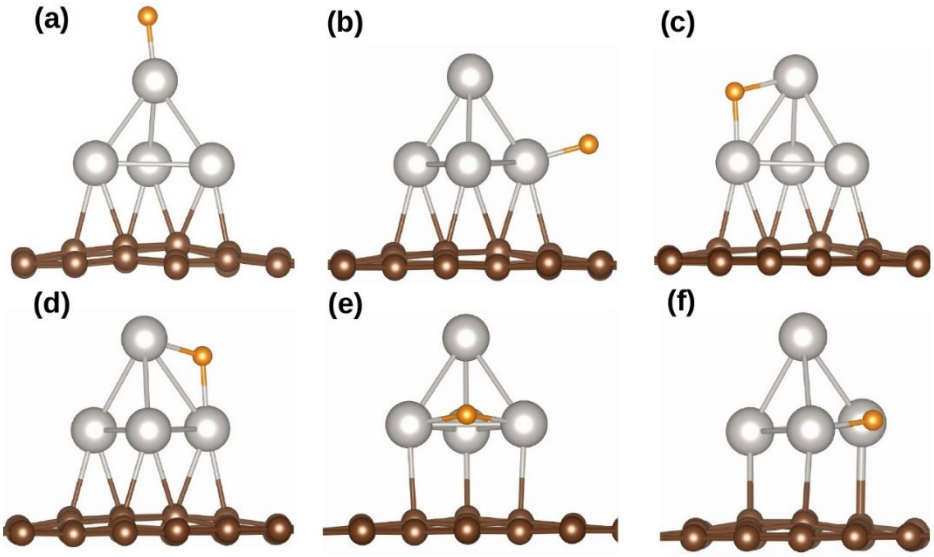


**Figure S11**: Optimized structures of a H atom adsorbed on $Pt_4$/graphene at different adsorption sites of $Pt_4$ cluster: (a) top; (b) top-interface; (c-d) bridge; (e-f) bridge-interface (Grey, Pt; Orange, H; Brown, C).

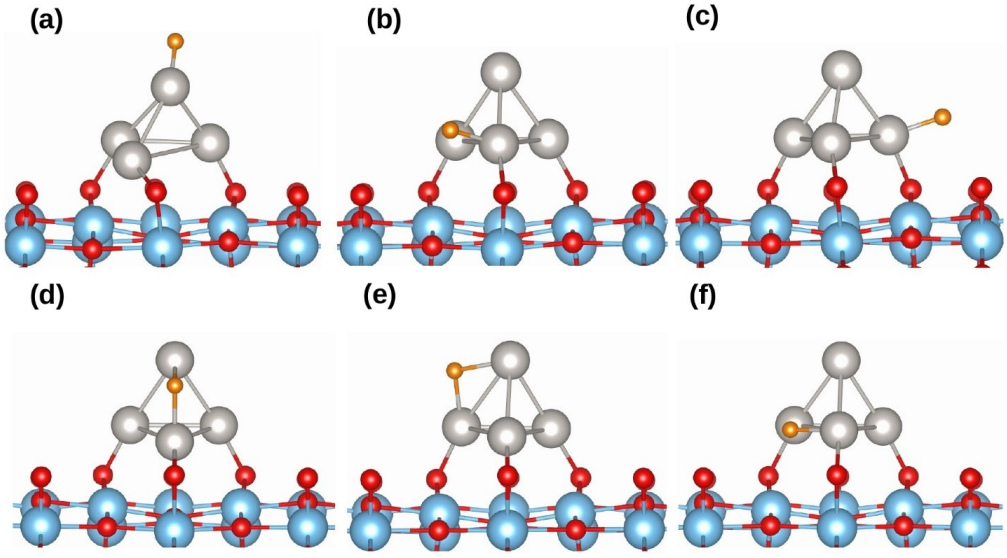


**Figure S12:** Optimized structures of a H atom adsorbed on $Pt_4$/anatase (101) at different adsorption sites of $Pt_4$ cluster: (a) top; (b-c) top-interface; (d-e) bridge; (f) bridge-interface (Grey, Pt; Orange, H; Blue, Ti; Red, O).

## 7. Multiple H adsorption on $Pt_4$/graphene and $Pt_4$/anatase (101) surfaces

### 7.1 One H atom adsorption on bare graphene and anatase (101) surfaces

To see the metal cluster effect on the H adsorption energy in the presence of $Pt_4$, we also explored atomic H adsorption on bare graphene and anatase (101) surfaces when assuming $H_2$ dissociative adsorption has already happened. An atomic H atom was adsorbed at C-top, C-C bridge and hollow sites of graphene as illustrated in Figure S13. Their corresponding adsorption energies and bond lengths in Table S2 reveal that the single H atom is unbound to the pristine graphene surface with endothermic adsorption energies of 1.38~2.48 eV and with H-C distance larger than 1.32 Å. Bader charge analysis in Table S2 demonstrates that H adsorbs on graphene and anatase (101) surfaces in the form of a neutral atom and a proton respectively.

As expected, for the strongest H adsorption site on anatase (101) surface is 2-fold coordinated oxygen atom ($O_{2c}$) with adsorption energy of -0.24 eV and H-O bond length of 0.98 Å (Figure 14a and Table S2), compared to those adsorbed on three-fold coordinated oxygen ($O_{3c}$) atom with $E_{ads}$ of 0.23 and 0.41 eV (Figures S14b and S14c, Table S2). For anatase (101), the adsorption of a H atom on anatase (101) leads to an electron transfer to the surface by forming hydroxyl group (-OH) which can be seen from Bader charges of H atom (+0.68 |e|) and anatase (101) (-0.68 |e|), reducing the $Ti^{4+}$ to $Ti^{3+}$.

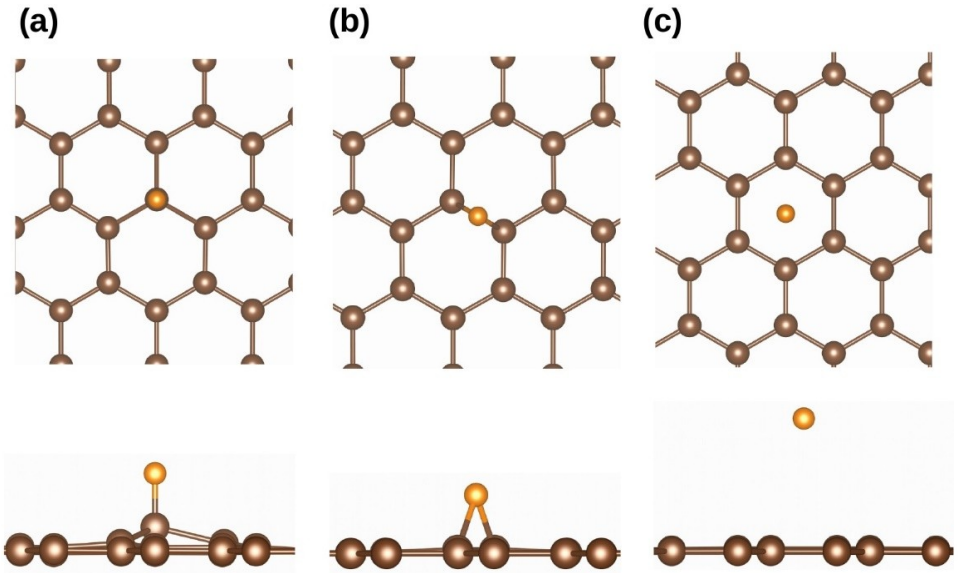


**Figure S13**: Optimized structures of a H atom adsorbed on graphene at different adsorption sites: (a) top; (b) bridge; (c) hollow (Orange, H; Brown, C).

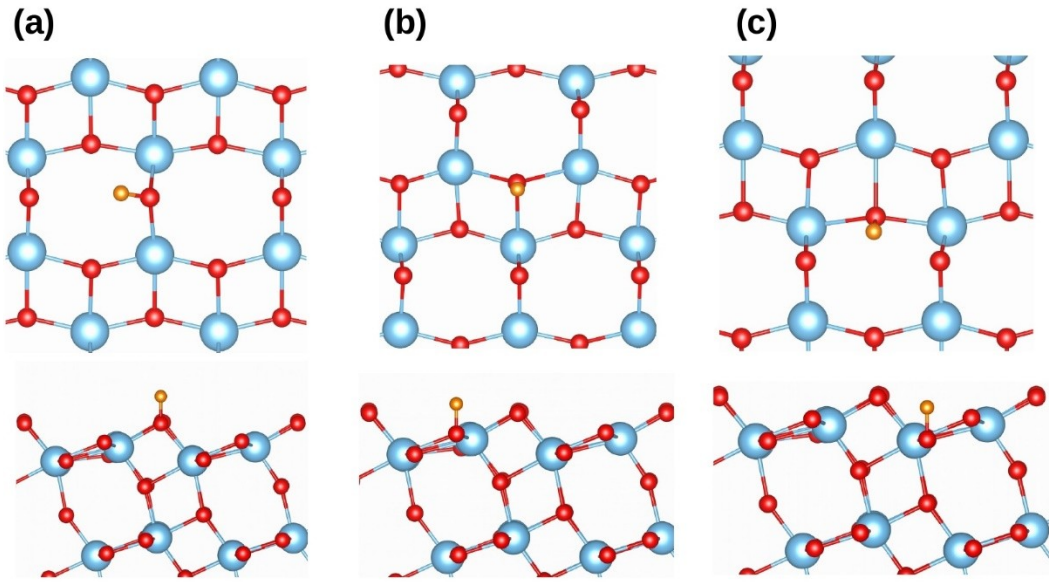


**Figure S14**: Optimized structures of a H atom adsorbed on anatase (101) surface at different adsorption sites: (a) $O_{2c}$; (b) $O_{3c}$; (c) $O_{3c}$ (Orange, H; Blue, Ti; Red, O).

**Table S2**: Adsorption energies, $E_{ads}$ (eV), average bond lengths, d(H-X) (Å) and Bader charge (|e|) of a H atom adsorbed on graphene and anatase (101) supports at different adsorption sites.

| System | Adsorption site | $E_{ads}$ (eV) | d(H-X) (Å) | Bader charge (\|e\|) | | Figure |
|---|---|---|---|---|---|---|
| | | | | H | Support | |
| H/Graphene | $C_{top}$ | 1.38 | 1.12[a] | 0.07 | -0.07 | S13a |
| H/Graphene | $C_{bridge}$ | 2.48 | 1.32[a] | 0.07 | -0.07 | S13b |
| H/Graphene | $C_{hollow}$ | 2.18 | 3.26[a] | 0.00 | 0.00 | S13c |
| H/Anatase | $O_{2c\ top}$ | -0.24 | 0.98[b] | 0.68 | -0.68 | S14a |
| H/Anatase | $O_{3c\ top}$ | 0.23 | 0.99[b] | 0.67 | -0.67 | S14b |
| H/Anatase | $O_{3c\ top}$ | 0.41 | 0.98[b] | 0.65 | -0.65 | S14c |

[a]The average H-C nearest neighbor distance. (X = C)

[b]The average bond length between H and O. (X = O)

### 7.2 Adsorption energy differences between non-spillover and spillover models

The energy differences between adsorption energy per H atom for non-spillover and spillover models were calculated to present an atomic H atom migration from $Pt_4$ surface to the supports of $Pt_4$/graphene and $Pt_4$/anatase (101), and a $H_2$ molecule migration to graphene of $Pt_4$/graphene in the aspect of thermodynamics (Figure S15). The results show that their energy differences for one H atom adsorption are large for $Pt_4$/graphene (1.84 eV) and small (0.14 eV) for $Pt_4$/anatase (101), implying that the migration of a H atom from $Pt_4$ to support is more likely to happen for $Pt_4$/anatase (101) at low H coverage.

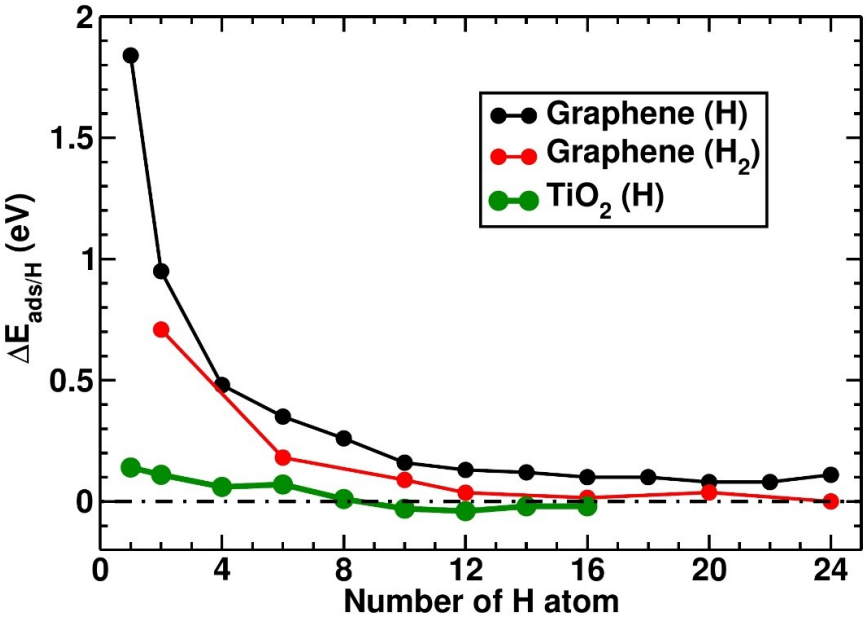


**Figure S15:** Energy differences of the adsorption energies per H atom between non-spillover and spillover models for $Pt_4$/graphene (H atom and $H_2$ molecule adsorption on the support) and $Pt_4$/anatase (101) surfaces.

## 8. H spillover barriers for $Pt_4$/graphene and $Pt_4$/anatase (101) surfaces

From the perspective of kinetics, the activation energy barriers for a single H migration from $Pt_4$ surface to the support of graphene and anatase (101) are 2.38 and 0.17 eV respectively when $Pt_4$ is saturated with 10H (in Figures 16 and 17).

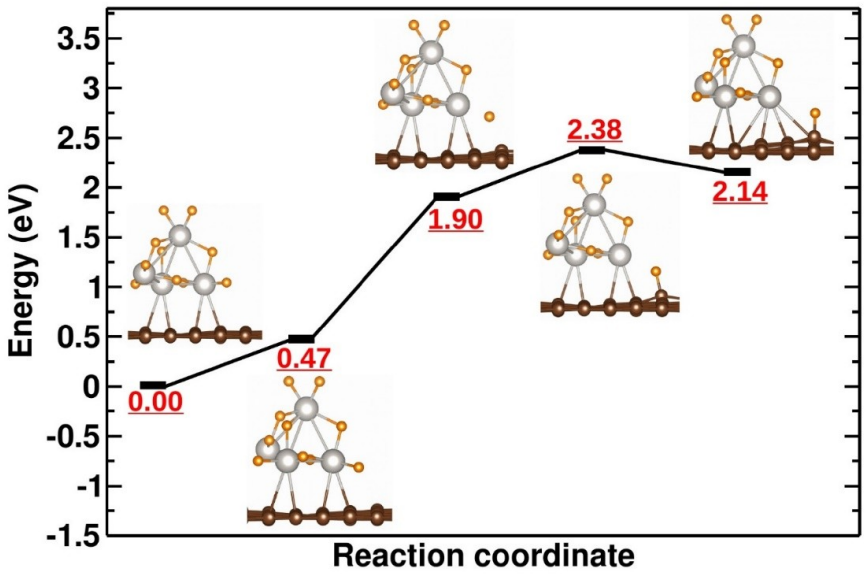


**Figure S16:** Energy profile for single H atom migration from $Pt_4$ cluster to graphene surface for 10H/$Pt_4$/Graphene (Grey, Pt; Orange, H; Brown, C).

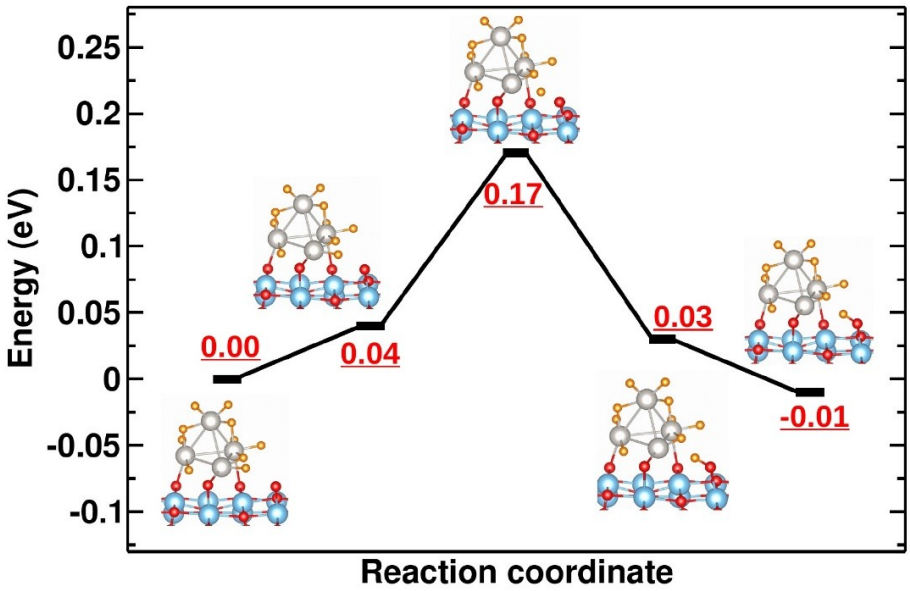


**Figure S17:** Energy profile for single H atom migration from $Pt_4$ cluster to anatase (101) surface for $10H/Pt_4/TiO_2$ (Grey, Pt; Orange, H; Blue, Ti; Red, O).

### 9. $H_2$ dissociative adsorption on freestanding $Pt_4$, $Pt_4$/graphene and $Pt_4$/anatase (101) surfaces

The adsorption energies per H atom of a single H atom and dissociative adsorption of multiple $H_2$ on freestanding $Pt_4$, $Pt_4$/graphene and $Pt_4$/anatase (101) are illustrated in Figure S18. H-Pt adsorption magnitude decreases on graphene and anatase (101) supported $Pt_4$ by 0.26 and 0.24 eV respectively with only one H adsorption. When 16 H atoms adsorb on $Pt_4$ and $Pt_4$/graphene and $Pt_4$/anatase (101), their values of $E_{ads/H}$ are -0.59, -0.52, -0.41 eV respectively.

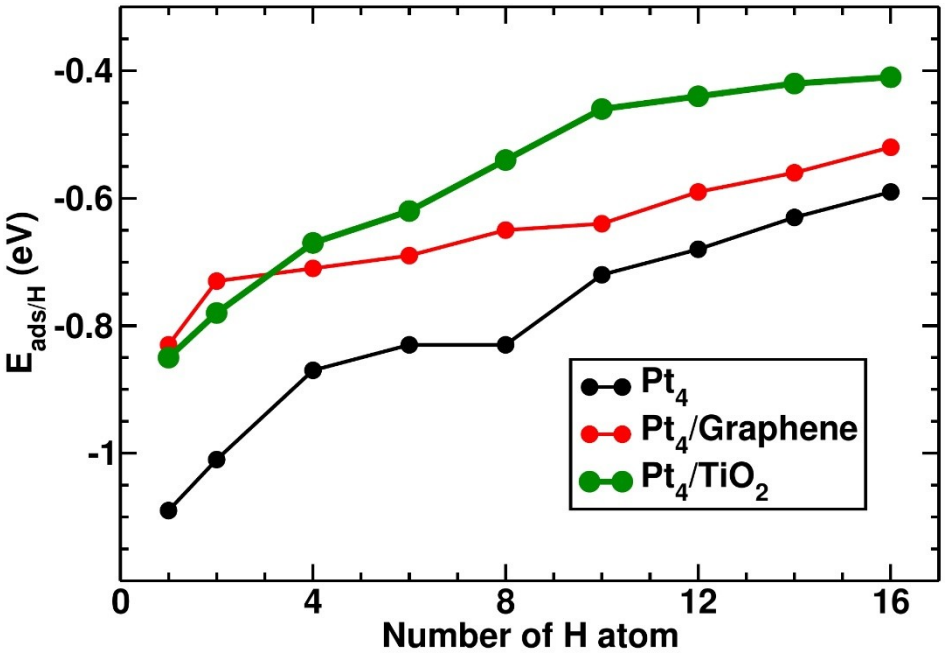


**Figure S18:** Adsorption energies per H atom for multiple H adsorption on freestanding $Pt_4$, graphene and anatase-$TiO_2$ (101) supported $Pt_4$.