# Supplementary materials

## 1.1 Hydrogen molecule sorption on h-BN monolayer and in h-BN bulk.

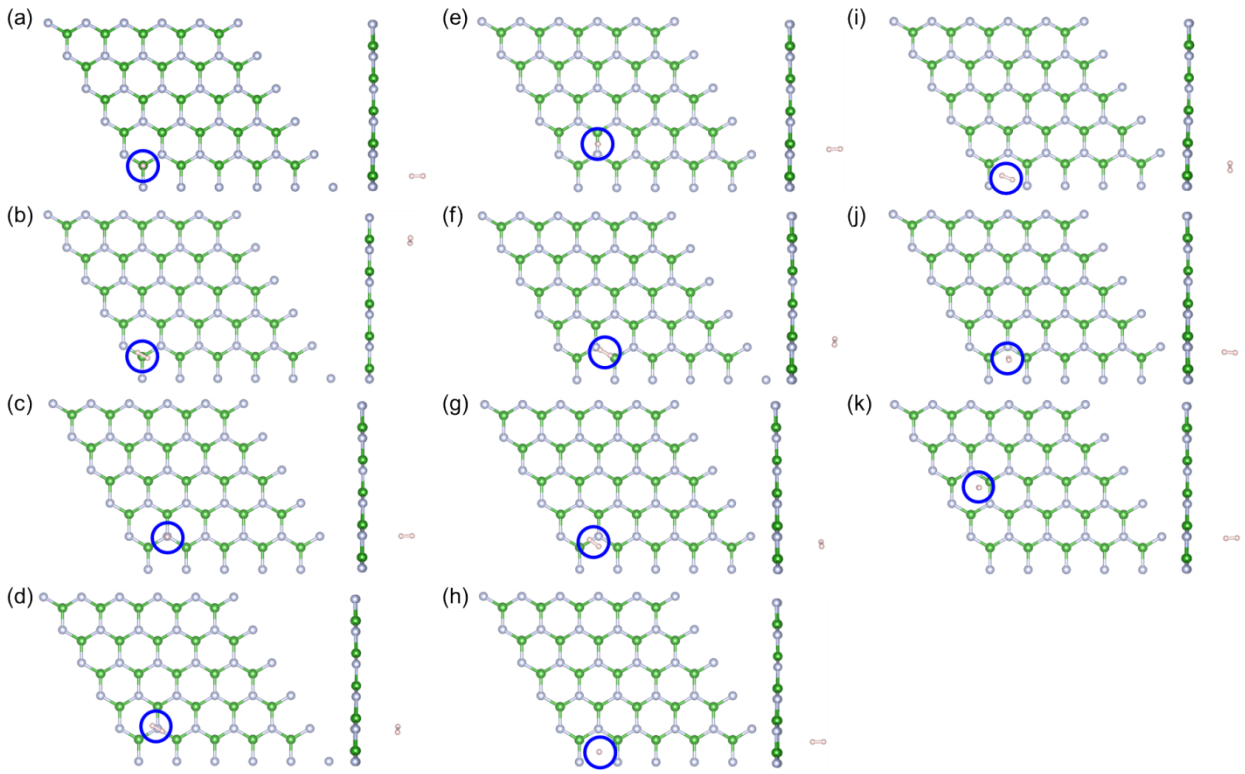


Figure S1. Considered positions of sorption of a single hydrogen molecule $H_2$ on the surface of a monolayer of hexagonal boron nitride. Gray, green, and pink colors indicate boron, nitrogen, and hydrogen atoms, respectively. The black lines indicate the unit cell of the considered structures. The blue circle indicates the position of the hydrogen molecule.

Table S1. Calculated values of the sorption energy per $H_2$ molecule ($E_{ads}^{H_2}$) and the sorption energy per h-BN unit ($\langle E_{ads}^{H_2} \rangle$) for each considered position of the hydrogen molecule.

| Position of the $H_2$ molecule | $E_{ads}^{H_2}$, $10^{-3}$ eV | $\langle E_{ads}^{H_2} \rangle$, $10^{-3}$ eV |
|---|---|---|
| (a) | -50.8 | -2.03 |
| (b) | -51.6 | -2.06 |
| (c) | -55.0 | -2.20 |
| (d) | -39.3 | -1.57 |
| (e) | -54.3 | -2.17 |
| (f) | -44.5 | -1.78 |
| (g) | -45.1 | -1.80 |

| | | |
|---|---|---|
| (h) | -49.3 | -1.97 |
| (i) | -55.1 | -2.20 |
| (j) | -49.4 | -1.98 |
| (k) | -55.3 | -2.03 |

1.2 The gravimetric storage density determination.

To calculate the value of gravimetric storage at which the sorption energy per h-BN unit becomes positive we plotted the line between closest to zero points. It should be noted that the obtained value depends on the choice of this points and in the case of h-BN monolayer varies from 5.31 to 5.46 wt.% and in the case of bulk h-BN - from 11.89 to 12.53 wt.%.

1.3 Hydrogen atom sorption on h-BN monolayer and in h-BN bulk.

Table S2. Calculated values of the H atom sorption energy for each considered position in the case of h-BN monolayer.

| Supercell | $E_{ads}^{H}$, eV/H | | |
|---|---|---|---|
| | On B atom | On N atom | On $B_3N_3$ hexagon |
| 2×2×1 | 2.43 | 3.09 | 3.15 |
| 5×5×1 | 2.57 | 3.41 | 3.40 |
| Mean $E_{ads}^{H}$ | 2.50 | | |

Table S3. Calculated values of the H atom sorption energy for each considered position in the case of h-BN bulk.

| Supercell | $E_{ads}^{H}$, eV/H | |
|---|---|---|
| | On B atom | On $B_3N_3$ hexagon |
| 3×3×1 | 2.53 | 3.31 |
| 3×3×2 | 2.61 | 3.36 |
| 4×4×1 | 2.51 | 3.28 |
| 4×4×2 | 2.60 | 3.39 |

| | | |
|---|---|---|
| 5×5×1 | 2.53 | 3.32 |
| 5×5×2 | 2.60 | 3.39 |
| Mean $E_{ads}^{H}$ | 2.56 | |

1.4 Hydrogen molecule diffusion on the surface of h-BN

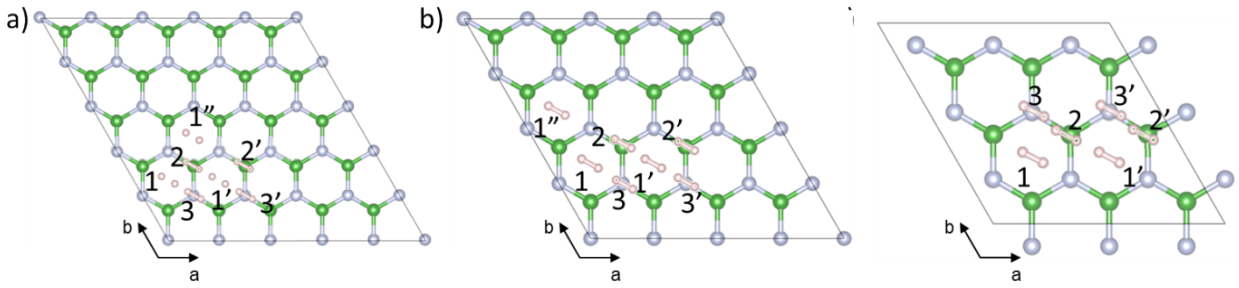


Figure S2. The considered positions of single $H_2$ molecule sorption with a parallel arrangement of the molecule relative to the h-BN monolayer surface: 1 – sorption near B atom, 2 – sorption on B atom, 3 – sorption on N. The considered supercell of a h-BN monolayer a) 5×5×1; b) 4×4×1; c) 3×3×1 containing one hydrogen molecule is indicated by black lines. Green, gray, and pink colors represent boron, nitrogen, and hydrogen atoms, respectively.

Table S4. Calculated values of diffusion barriers of an individual $H_2$ molecule with a parallel arrangement of the molecule relative to the h-BN monolayer surface

| Supercell | 5×5×1 | | 4×4×1 | | 3×3×1 | |
|---|---|---|---|---|---|---|
| ω, % | 0.32% | | 0.51% | | 0.89% | |
| Diffusion path | $E_b$, $10^{-3}$ eV | | $E_b$, $10^{-3}$ eV | | $E_b$, $10^{-3}$ eV | |
| | Direct | Reverse | Direct | Reverse | Direct | Reverse |
| 1→1’ | 11.1 | 11.1 | 10.6 | 7.2/3.4 | 16.3 | 16.3 |
| 1→1” | 7.9 | 7.9 | 7.4/3.4 | 7.4 | 17.7 | 17.7 |
| 1→2 | 6.7 | 0.0 | 2.7 | 0.3/0.8 | 16.3 | 12.7 |
| 1→3 | 16.6 | 0.0 | 10.7 | 0.0 | 15.7 | 0.5 |
| 2→3 | 9.5 | 0.0 | 11.1 | 2.1 | 11.3 | 2.7 |
| 2→2’ | 6.7 | 6.7 | 3.9/2.1 | 6.0 | 5.0 | 5.0 |
| 3→3’ | 15.7 | 15.7 | 14.7 | 14.7 | 16.6 | 16.6 |

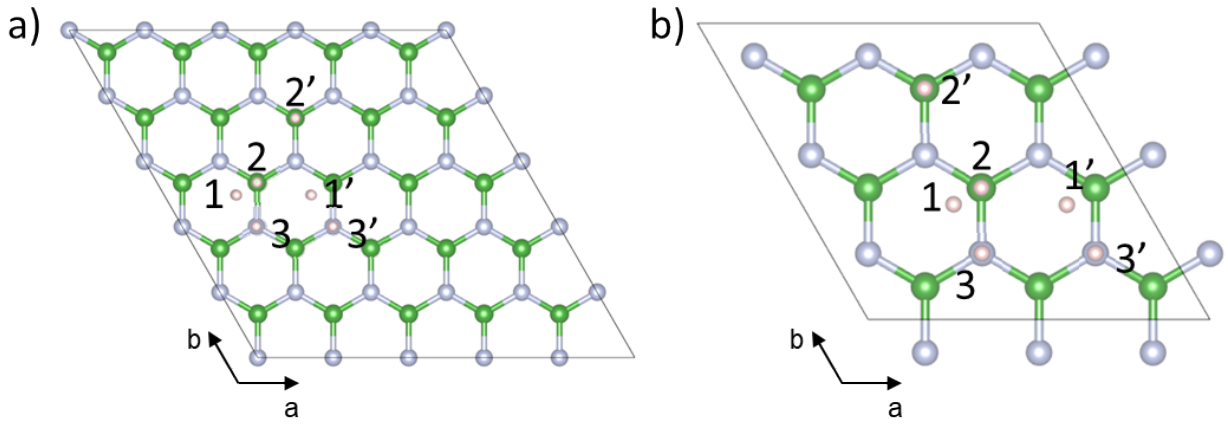


Figure S3. The considered positions of single $H_2$ molecule sorption with a perpendicular arrangement of the molecule relative to the h-BN monolayer surface: 1 – sorption near B atom, 2 – sorption on B atom, 3 – sorption on N. The considered supercell of a h-BN monolayer a) 5×5×1; b) 3×3×1 containing one hydrogen molecule is indicated by black lines. Green, gray, and pink colors represent boron, nitrogen, and hydrogen atoms, respectively.

Table S5. Calculated values of diffusion barriers of an individual $H_2$ molecule with a perpendicular arrangement of the molecule relative to the h-BN monolayer surface

| Supercell | 5×5×1 | | | 3×3×1 | | |
|---|---|---|---|---|---|---|
| ω, % | 0.32% | | | 0.89% | | |
| Diffusion path | $E_b$, $10^{-3}$ eV | | | $E_b$, $10^{-3}$ eV | | |
| | Direct | | Reverse | Direct | | Reverse |
| 1→1' | 5.1 | 3.1 | 8.2 | 1.6 | 1.6 | 3.1 |
| 1→2 | 5.0 | | 0.1 | 2.2 | | 0.0 |
| 1→3 | 0.1 | | 1.3 | 0.0 | | 1.4 |
| 2→3 | 0.0 | | 6.1 | 0.0 | | 3.6 |
| 2→2' | 7.1 | | 7.1 | 3.4 | | 3.4 |

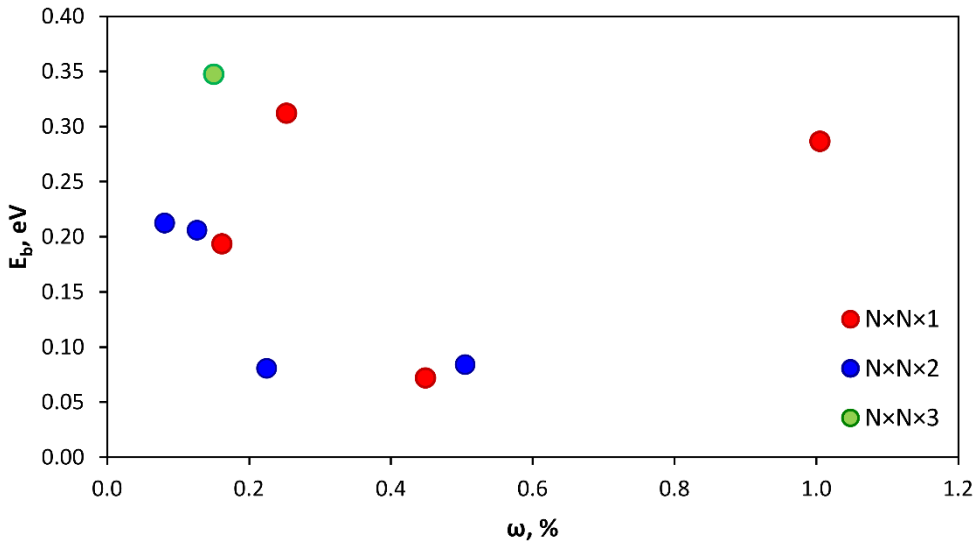


Figure S4. Dependence of the diffusion barrier of a single $H_2$ hydrogen molecule in parallel to monolayers surface direction between the centers of neighboring $B_3N_3$ rings in h-BN bulk crystal represented by N×N×z supercell (z=1 (red), 2 (blue), 3(green)) on the gravimetric density.

1.5 Hydrogen molecule diffusion through the surface of h-BN

Table S6. The calculated diffusion barriers values of a hydrogen molecule through a h-BN monolayer for the various considered supercells of hexagonal boron nitride.

| Supercell | 4×4×1 | 2×2×1 | 3×3×1 | 4×4×1 | 5×5×1 |
|---|---|---|---|---|---|
| N[$H_2$] | 16 | 1 | 1 | 1 | 1 |
| $E_b$, eV | 10.42 | 11.73 | 10.00 | 10.79 | 10.41 |
| ω, % | 7.51 | 1.99 | 0.89 | 0.51 | 0.32 |

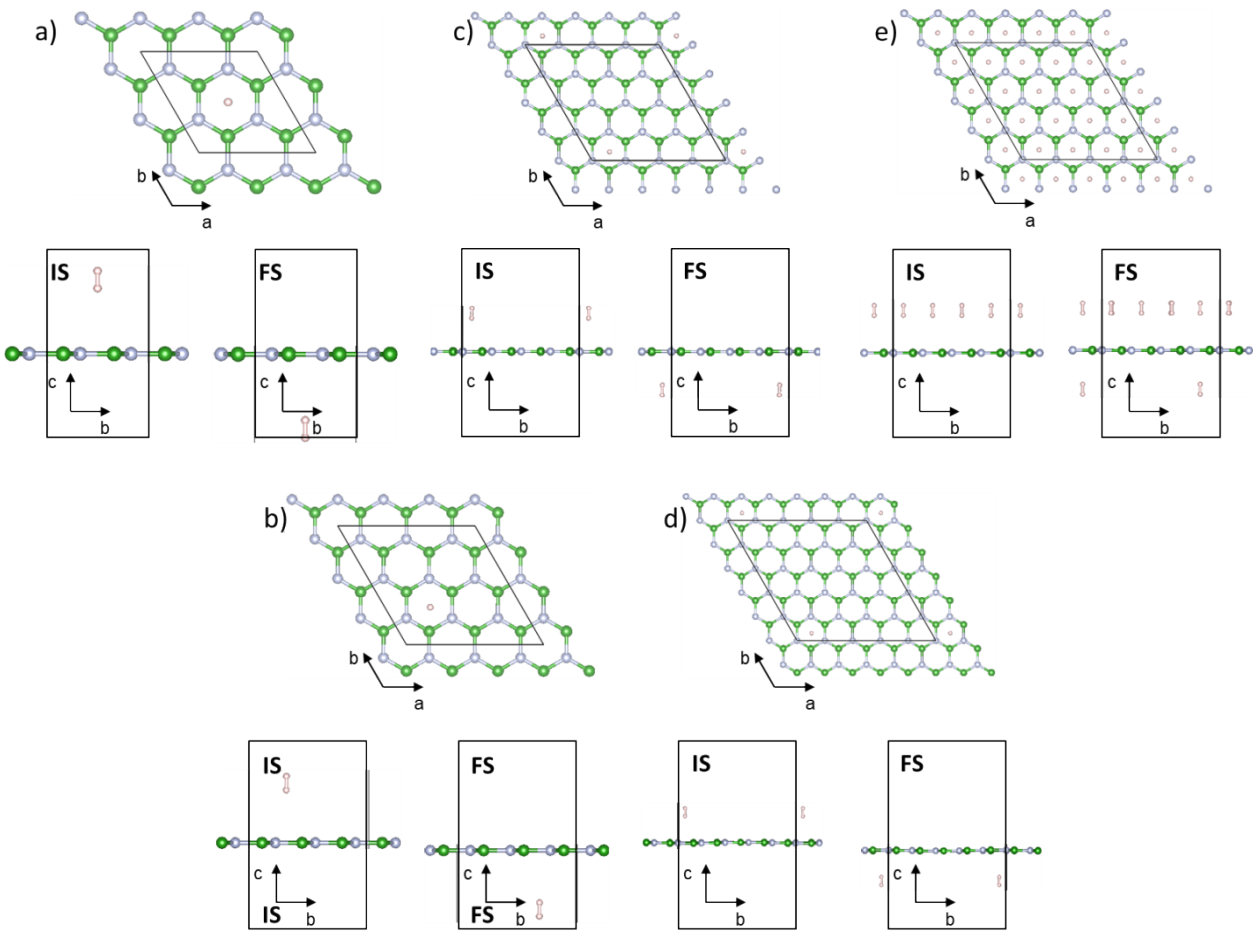


Figure S5. Considered supercells, initial (IS) and final (FS) positions of single hydrogen molecule diffusion through a h-BN monolayer: a) 2×2×1 supercell with one hydrogen molecule; b) 3×3×1 supercell with one hydrogen molecule; c) 4×4×1 supercell with one hydrogen molecule; d) 5×5×1 supercell with one hydrogen molecule, d) 4×4×1 supercell with 16 hydrogen molecules located on one side of the monolayer. Supercells of a hexagonal boron nitride monolayer are indicated by black lines. Green, gray, and pink colors represent boron, nitrogen, and hydrogen atoms, respectively.

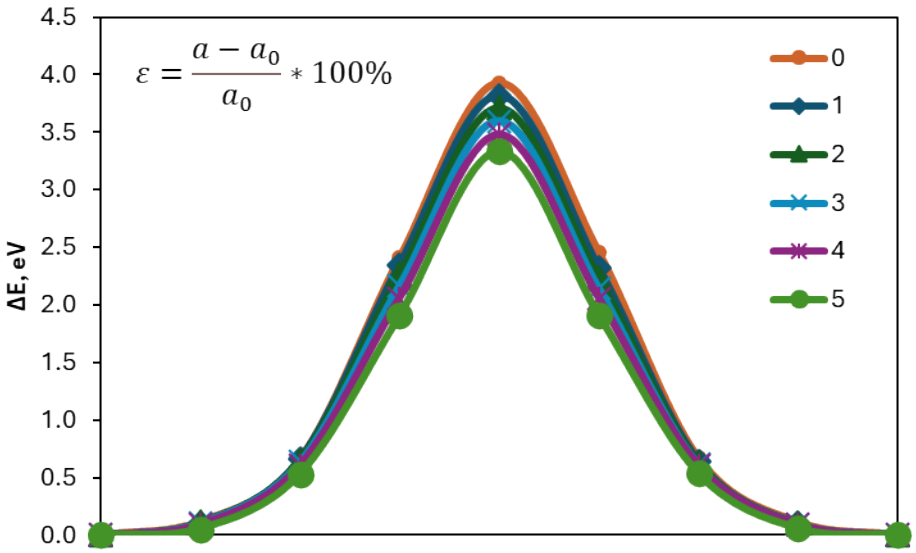


Figure S6. Energy profile of the reaction of atomic hydrogen diffusion through a biaxially stretched monolayer of hexagonal boron nitride h-BN for different values of $\varepsilon$ ranging from 0 to 5%.

Table S7. Calculated barrier values of physiosorbed atomic hydrogen for diffusion through h-BN monolayer in the case of biaxially stretched h-BN monolayer.

| $\varepsilon$, % | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| $E_b$, eV | 3.93 | 3.82 | 3.71 | 3.60 | 3.48 | 3.34 |