Supplementary Information

First principles guide to tune *h-BN* nanostructures as superior light element based hydrogen storage material: Role of bond exchange spillover mechanism

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System	Formation Energy (eV)
CBN (B site)	1.159
CBN (N site)	6.529
OBN (B site)	5.002
OBN (N site)	1.742
COBN (para)	2.178
COBN (ortho)	3.081
COBN (far)	2.278

Table S1: Formation energy per supercell of doped h-BN sheet with different type of configuration. Gray color shading indicates the most favorable doping configuration.

Formation Energy can be defined as

$$E_{for} = E_{total}\,(doped) - E_{total}\,(h\text{-}BN) + n_B\mu_B + n_N\mu_N - n_C\mu_C - n_O\mu_O$$

E_{tot}(doped) and E_{tot}(h-BN) are the total energies of a doped and pure h-BN monolayer, respectively. n_B and n_N, is the number of boron and nitrogen atoms replaced per unit supercell, and n_C, n_O are the number of carbon, oxygen dopant atoms per unit supercell. The chemical potentials (μ) of elements depend on the experimental conditions. We assume a nitrogen-rich environment, assuming that the h-BN is grown in thermal equilibrium with the N_2 molecular gas. Therefore, we take $\mu_N = (1/2)\mu_{N_2\ gas}$, $\mu_O = (1/2)\mu_{O_2\ gas}$, and $\mu_B = \mu_{BN} - \mu_N$. The μ_C is evaluated from the total energy of graphite per C atom.

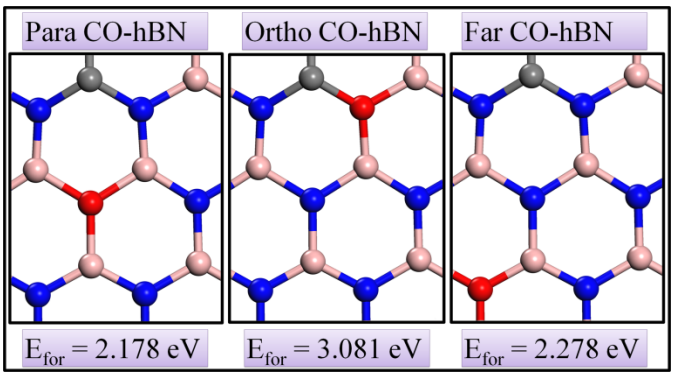

Fig. S1. The structure and the formation energy of the three different configuration of C-O co-doped h-BN sheet.

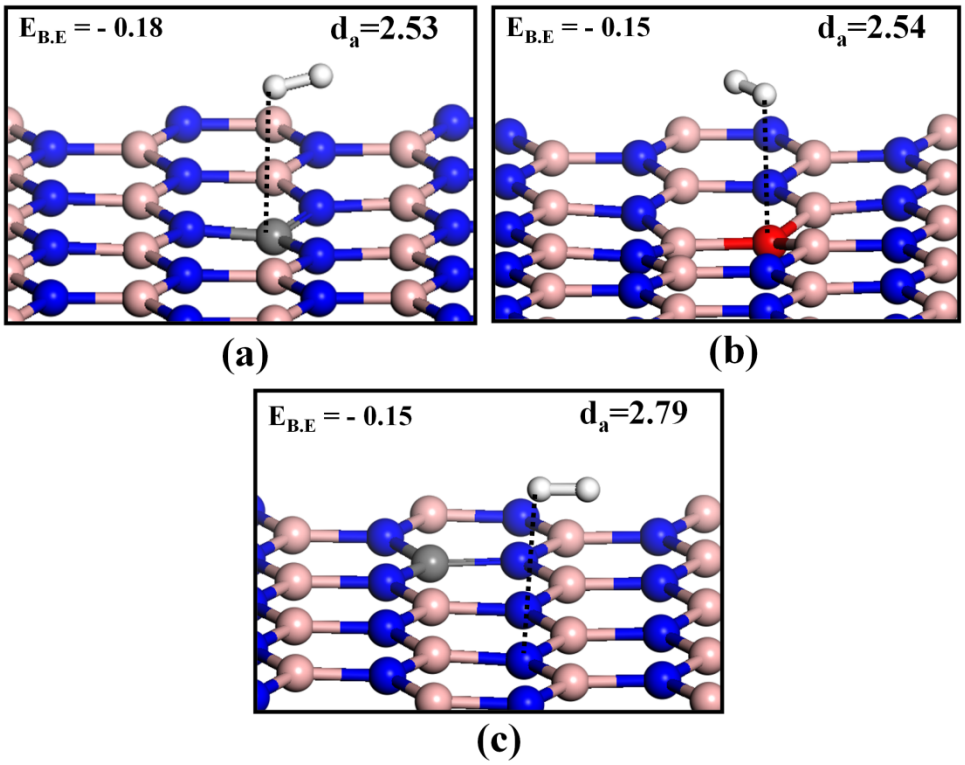

Fig. S2 Optimized structures of single H_2 adsorbed on (a) C atom of C-doped h-BN surface, (b) O atom of O-doped h-BN surface and (c) N atom of C-doped h-BN surface. The red, gray, pink and blue balls represent the oxygen, carbon, boron and nitrogen atoms. Hydrogen molecule is represented by white ball. Binding energies ($E_{B.E}$) are in eV. H_2-surface distances (d_a) are in Å. Black dotted line is for guide to the eye to show nearest active sites.

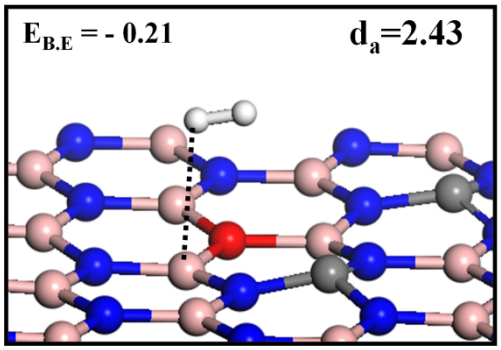

Fig. S3 Single H_2 molecule adsorbed on B atom of 2COBN surface. Atomic symbols follow the same convention used in Figure S1. Binding energy ($E_{B.E}$) is in eV. H_2-surface distance (d_a) is in Å. Black dotted line is for guide to the eye to show nearest active site.

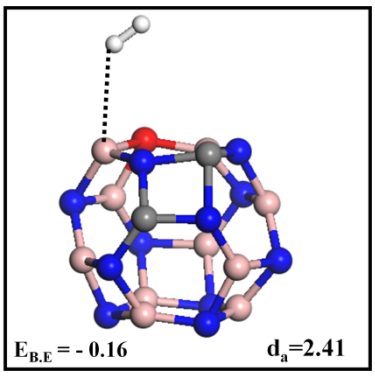

Fig. S4 Single H_2 molecule adsorbed on B atom of $2COB_{10}N_{11}$ nanocage. Atomic symbols follow the same convention used in Figure S1. Binding energy ($E_{B.E}$) is in eV. H_2-surface distance (d_a) is in Å. Black dotted line is for guide to the eye to show nearest active site.

H_2 molecule interacts with the surface more strongly when we increase the percentage of doping in the h-BN surface. Binding energy value reaches to 0.50 eV for 12.5 % of C-O doping. The binding value increases more with the doping percentage.

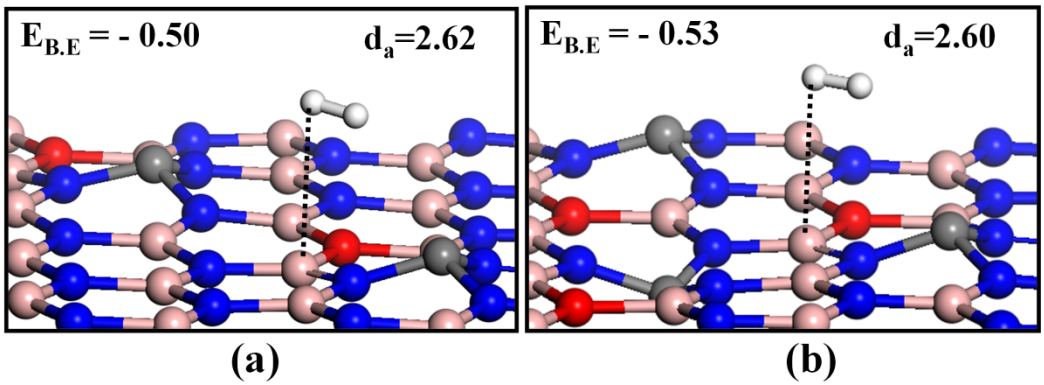

Fig. S5 Optimized geometries of single H_2 interaction on two different surfaces (a) 2C2OBN and (b) 3C3OBN. Atomic symbols follow the same convention used in Figure S1. Binding energies ($E_{B.E}$) are in eV. H_2-surface distances (d_a) are in Å. Black dotted line is representing the minimum distance between H_2 and surface.

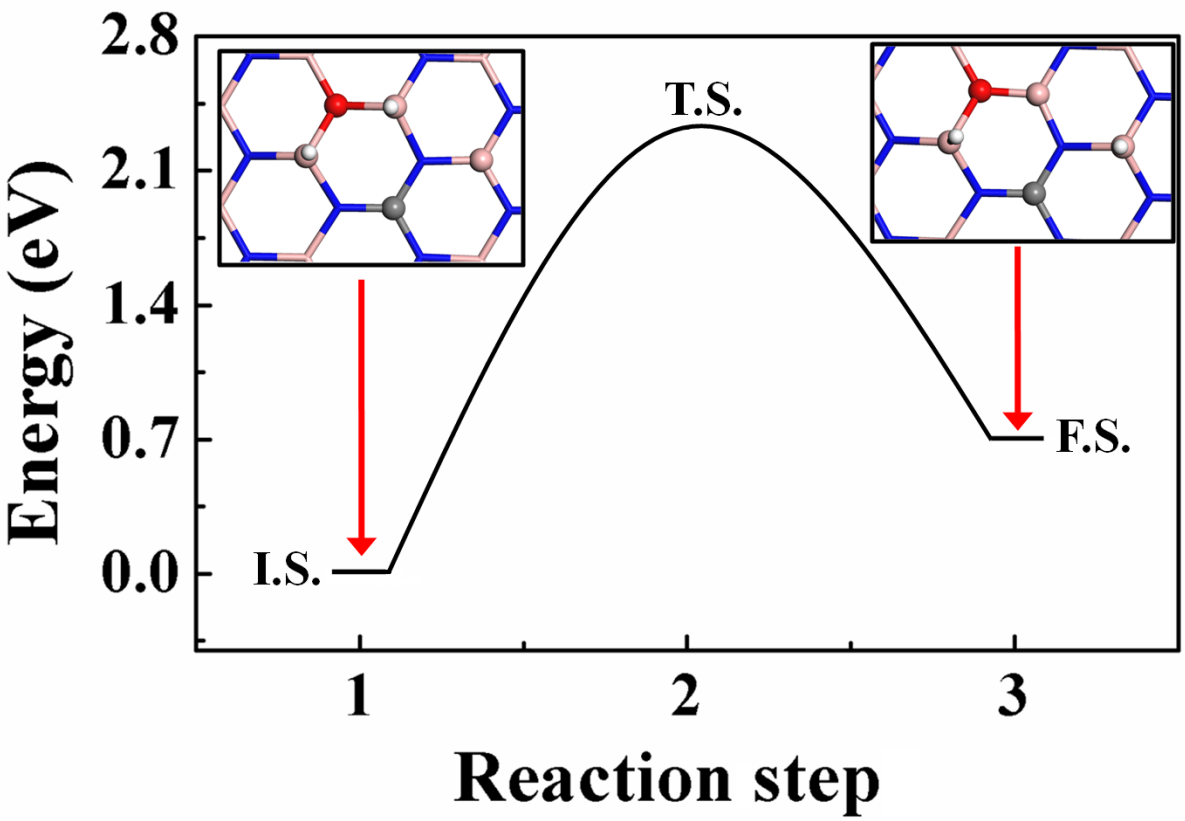

Fig. S6 The barrier energy curve during the migration of H atom from the dissociated H_2 configuration on COBN surface. The inset shows the relaxed structure of initial state (I.S.) and Final state (F.S.). The black line connecting I.S., T.S. and F.S. are only for guide to the eye.

The bond exchange spillover can be realize only when the external agent is good enough in withdrawing the hydrogen atom from the surface (hydrogenated part) and also can donate the hydrogen to the surface with very low energy barrier (we found Gallene and Borane are the prominent molecule for the purpose). We also test the possibility of bond exchange spillover of H atom using ammonia (NH_3) and silane (SiH_4) molecules. We found that these molecules are not suitable as secondary catalyst. In case of NH_3 both withdrawn and release of hydrogen are forbidden. We got similar results on considering SiH_4 as the external mediator.

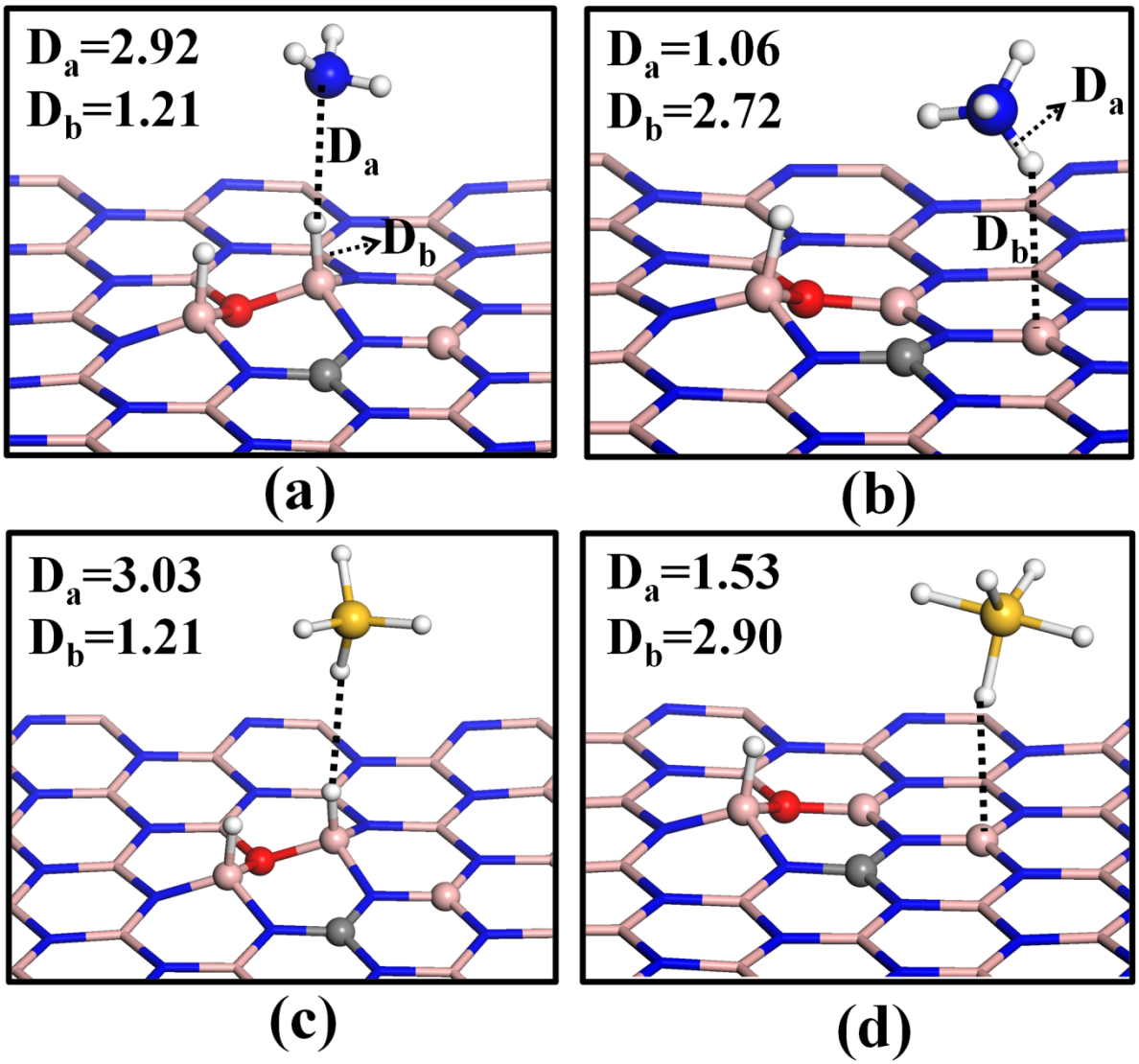

Fig. S7 The optimized structure of probable initial state (IS) {(a) & (c)} and final state (FS) {(b) & (d)} during bond exchange mechanism by means of ammonia (NH_3) and silane (SiH_4) as external mediator. The white, red, gray, pink, blue and yellow balls represent the hydrogen, oxygen, carbon, boron, nitrogen and silicon atoms. Distances are in Å.