Detailed explanations of the calculated data in Table I.

For simulating the full hydrogenation process, we modelled the BNC_H molecules by putting one H atom on each site of the nanocage as our initial structures, where the distance between the H atom and the site is set to be 1 Å. To study the thermodynamic quantities, Gibbs free energy *G*, enthalpy *H*, entropy *S*, and heat capacity c_v of each structure are calculated with the consideration of the contribution from the vibration. Since the theoretical calculation usually gives a relative overestimation to the vibrational modes, a frequency scaling factor of 0.96 was adopted for thermal energy corrections from the vibration of chemical bonds, in order to compare with the experimental results. Then, with standard thermodynamics theory, we can evaluate the thermodynamic properties of each structure under different temperature and pressure conditions.

ΔG_1 is the Gibbs free energy change per mole of H_2 gas absorbed at 10 bar and 25 ℃ in reaction (1), calculated as below:

$$\Delta G_1 = \left[G(\mathrm{BNC_H}) - G(\mathrm{BNC}) - nG(\mathrm{H_2})\right]/n, \quad \text{(S1)}$$

where *n* is the number of H_2 molecules. ΔG_2 is the Gibbs free energy change per mole of H_2 released at 1 bar and 100 ℃ in reaction (2):

$$\Delta G_2 = \left[G(\mathrm{BNC}) + nG(\mathrm{H_2}) - G(\mathrm{BNC_H})\right]/n. \quad \text{(S2)}$$

ΔG is the Gibbs free energy change for the dehydrogenation reaction calculated at 25 ℃ and 1 bar via Eq. (S2). In our case, for the full hydrogenated fullerene, *n* equals 12, and the calculated Gibbs free energy change per mole of H_2 is actually an average value of the reaction.

The changes of enthalpy ΔH_e and entropy ΔS_e per mole of H_2 molecules released at the equilibrium temperature T_e are calculated according to Ellingham approximation:

$$\Delta H_e = \Delta H(298) + (\Delta c_v/n + R)\,(T_e - 298), \quad \text{(S3)}$$

$$\Delta S_e = \Delta S(298) + (\Delta c_v/n + R)\ln\left(T_e/298\right), \quad \text{(S4)}$$

where R = 8.314 J/mol-K, $\Delta H(298)$, $\Delta S(298)$ and Δc_v are respectively the changes of enthalpy, entropy and total heat capacity at 25 ℃ and 1 bar, calculated in a dehydrogenation reaction. Since the Gibbs free energy change equals zero at T_e, we can have $T_e \approx \Delta H_e / \Delta S_e$.

Totally 24 H atoms chemisorbed on the outside of $B_{11}N_{12}C$, so 24H/(24H+12N+11B+C)*100
wt%=24*1.007825/(1.007825*24+14.003074*12+11.0093053*11+12)*100
wt%=7.43 wt%.

Fig. S1. $(BN)_{12}$ fullerene with an overall symmetry of T_h, composed of six squares and eight hexagons. All B sites are equivalent, so are all N.

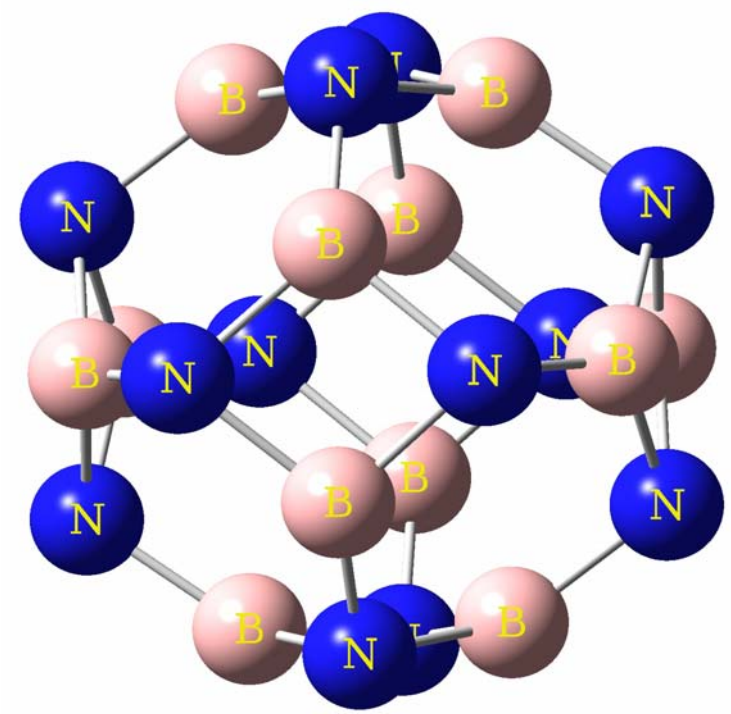
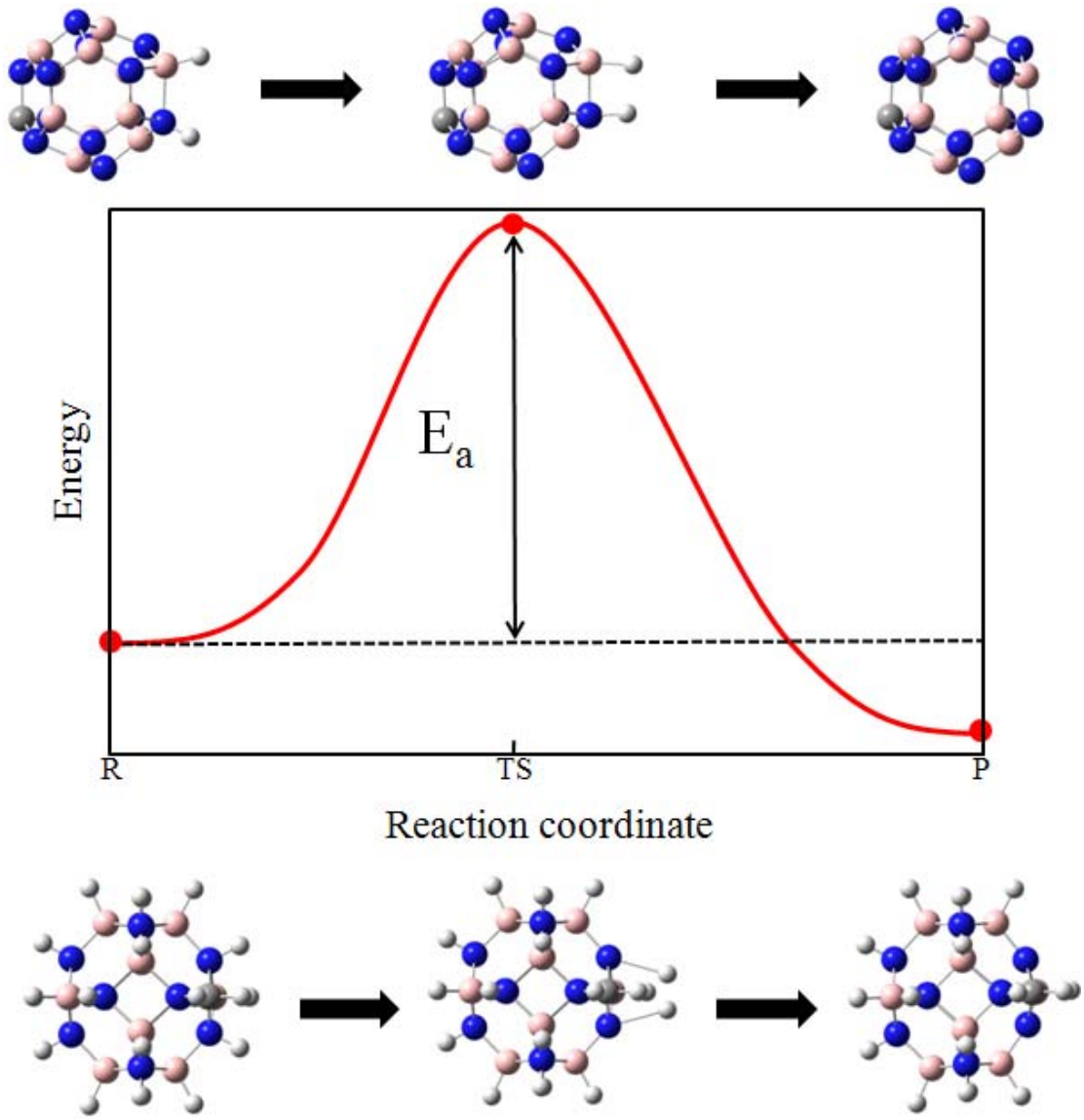


Fig. S2. Schematic diagram of activation energy E_a for the H_2 release reaction of $B_{11}N_{12}C$. Critical point structures are shown at the top and bottom. (H: white; B: pink; C: grey; N: blue.) The calculated E_a for the H_2 release from $B_{11}N_{12}C$-2H and full hydrogenated $B_{11}N_{12}C$ is 2.03 eV and 2.40 eV, respectively. The energy of product with respect to reactant is estimated to be -0.26 eV and -1.71 eV respectively for the top and bottom cases.



As seen from Fig. S2, from the starting reactants (R) to the final products (P), there exists a transition state (TS). The energy difference between R and TS is the activation energy for the reaction. For the hydrogen absorption process, as the H_2 molecule approaches the $B_{11}N_{12}C$, the two H atoms separate gradually due to the interaction with the BNC, and the corresponding activation energy E_a for the hydrogenation reaction is estimated to be 2.14 eV ($(BN)_{12}$: 1.83 eV), with the TS

structure having one imaginary frequency checked through the frequency calculations. The corresponding reverse barrier for the dehydrogenation process (top of Fig. S2) is also estimated to be 2.03 eV for $B_{11}N_{12}C$. For the hydrogen release process (bottom of Fig. S2), two H atoms move apart from the full hydrogenated $B_{11}N_{12}C$ and form the H_2 molecule in the distance, with the activation energy E_a of about 2.40 eV ($(BN)_{12}$: 5.66 eV) for the dehydrogenation reaction. The reverse barrier in this case is estimated to be 3.96 eV for $B_{11}N_{12}C$. Obviously, the C atom acts as an activation center for the dehydrogenation reaction, where H atoms on the N sites close to C are easier to release due to the electron transfer from C to N.

For the dehydrogenation reaction of the full hydrogenated $B_{11}N_{12}C$ (bottom of Fig. S2), the energy of product with respect to reactant is estimated to be -1.71 eV, while it is 2.38 eV for the hydrogen release process of the full hydrogenated $(BN)_{12}$ fullerene. It is obvious that the incorporation of C atom into the $(BN)_{12}$ fullerene makes the dehydrogenation reaction become thermodynamically favored, whereas it is quite difficult for $(BN)_{12}$ fullerene to dehydrogenate. Noticeably, as the hydrogen release process proceeds, the height of activation barrier gradually decreases, and the energy difference between product and reactant is also reduced, which is estimated to be -0.26 eV for two H atoms released from $B_{11}N_{12}C$ (top of Fig. S2). Therefore, the dehydrogenation process can proceed all the way for $B_{11}N_{12}C$.

Unfortunately, it is found that the adjacent-site absorption reaction for pristine $(BN)_{12}$ is 0.04 eV and it is 0.11 eV for $B_{11}N_{12}C$, where C-doping on $(BN)_{12}$ seems to be of no help for the hydrogenation reaction. Thus, for the hydrogen absorption process, higher pressure (>10 bar) may be needed. However, it should be noted that our calculation is based on H_2 molecule, which has a much lower energy than that of H atom. So if H atom is used as the reactant or H_2 molecule is activated under some reaction environment, the hydrogenation reaction will certainly be thermodynamically favored. In addition, since the activation energy may change with different hydrogen coverage, more investigations on the activation barrier are certainly needed in the future.