Electronic Supplementary Information

B_{12}-containing Volleyball-like Molecule for Hydrogen Storage

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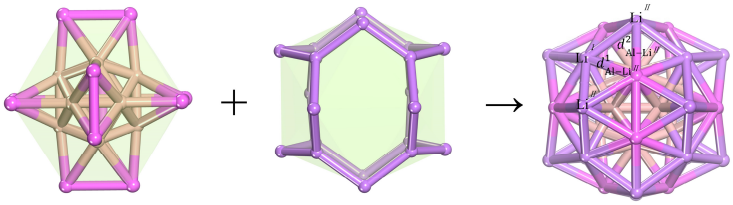


Fig. S1. The construction process of the core-shell volleyball-like $B_{12}@Li_{20}Al_{12}$. Here, 12 Al atoms (magenta) are located above the center of 12 triangles of the B_{12} icosahedron (pink), then every 2 Al atoms connect with 8 Li atoms (purple). The shell structure is like a volleyball consisting of six Al_2Li_8 subunits.

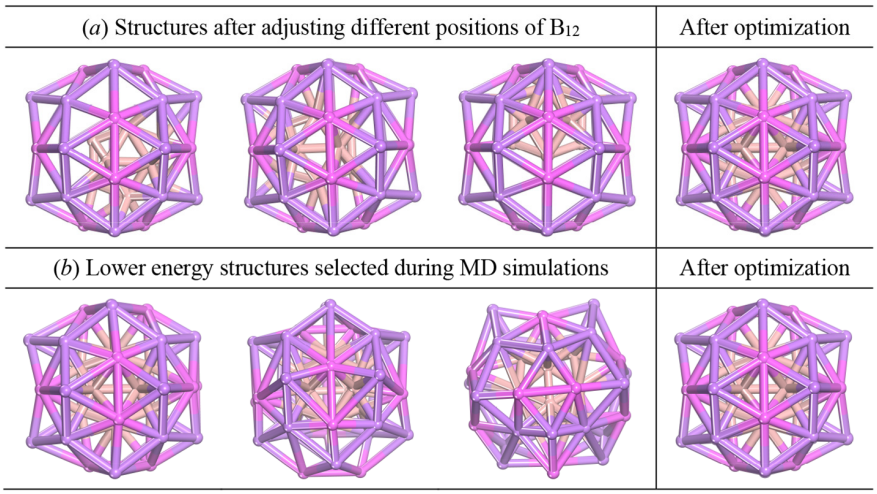


Fig. S2. (*a*) The optimized structures of the core-adjusted $B_{12}@Li_{20}Al_{12}$, and (*b*) low-energy $B_{12}@Li_{20}Al_{12}$ during MD simulations.

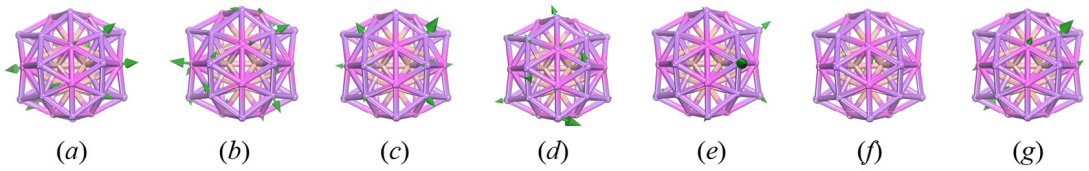


Fig. S3. Several vibrational frequency modes of the core-shell $B_{12}@Li_{20}Al_{12}$. To be specific, (*a*)-(*e*) correspond to the vibrational frequency modes for the peaks of 91.94 cm^{-1}, 157.87 cm^{-1}, 280.66 cm^{-1}, 355.68 cm^{-1} and 558.82 cm^{-1} respectively; (*f*)-(*g*) correspond to the vibrational frequency modes for the highest and lowest frequencies, respectively.

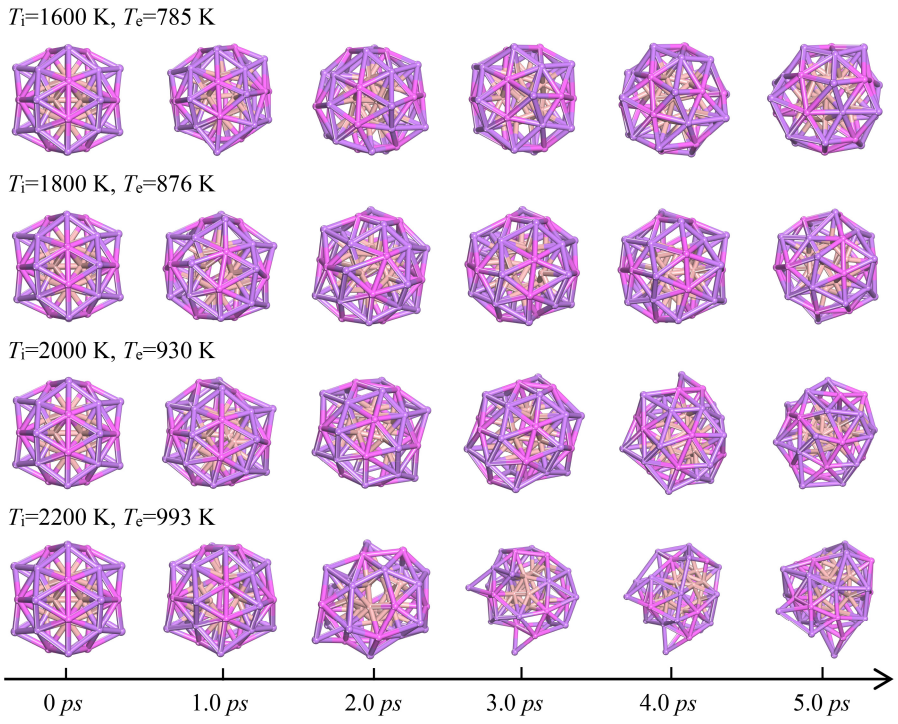
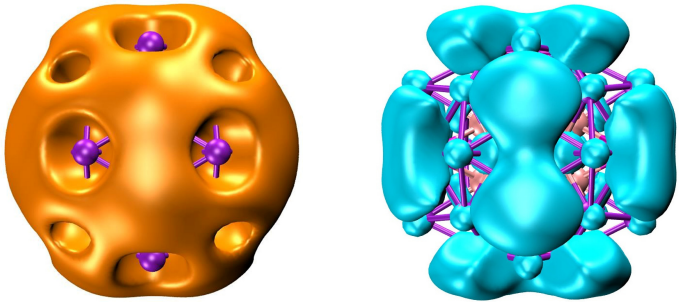


Fig. S4. Specific steps of the MD simulations at initial temperatures (T_i) of 1600 K, 1800 K, 2000 K and 2200 K for the core-shell $B_{12}@Li_{20}Al_{12}$. The corresponding effective temperatures (T_e) are also listed.



(*a*) (*b*)

Fig. S5. Isosurface of the localized orbital locator (LOL) and the electron localization function (ELF) for the $B_{12}@Li_{20}Al_{12}$ viewed from the top of the Al_2Li_8 subunit. The isovalues are 0.3 e/Å^3 and 0.7 e/Å^3 respectively.

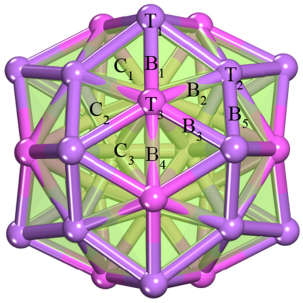
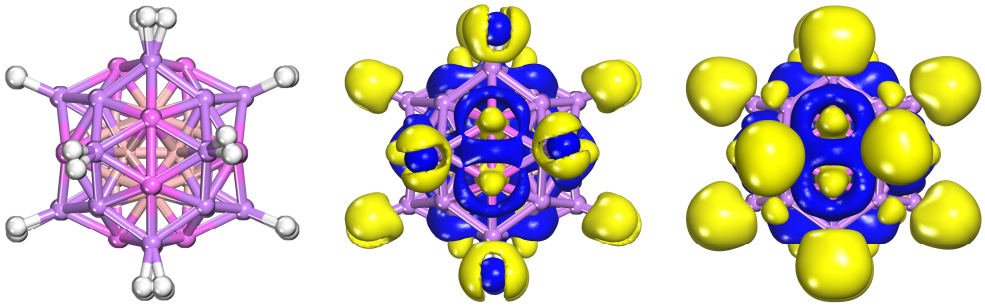
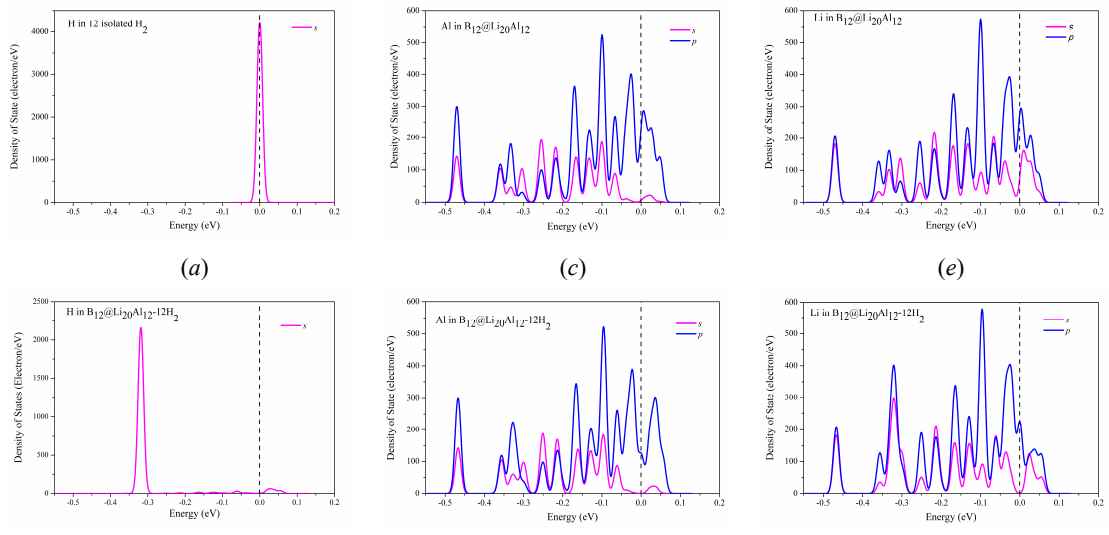


Fig. S6. Several possible locations of absorbed H_2 molecules. Specifically, T_1 and T_2 symbolize the top locations above the two types of Li atoms, T_3 symbolizes the top location above the Al atom; B_1, B_2 and B_3 symbolize the bridge locations above the Al-Li bonds, B_4 and B_5 symbolize the bridge locations above the Li-Li bond and Al-Al bond; C_1 and C_2 symbolize the top locations above the center of triangles composed of Al-Li-Li, C_3 symbolizes the top locations above the center of triangle composed of Li-Al-Al.



(*a*) (*b*) (*c*)

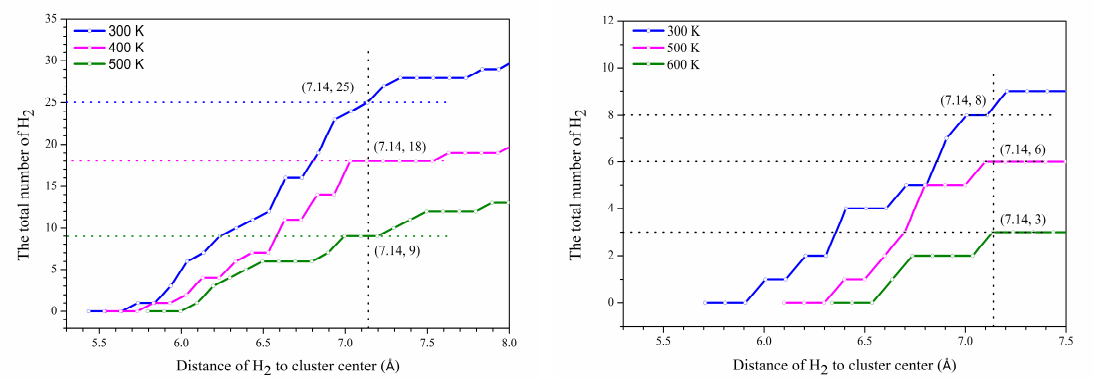
Fig. S7. The configuration of core-shell volleyball-like $B_{12}@Li_{20}Al_{12}$ with 12 H_2 absorbed on the 12 Li^{II} atoms ($B_{12}@Li_{20}Al_{12}$-$12H_2$) for part (*a*) and corresponding deformation electron density with different isovalues for part (b) and part (c). To be specific, the isovalue is 0.2 *e*/Å^3 for part (*b*) and 0.1 *e*/Å^3 for part (*c*).



(*a*) (*c*) (*e*)

(*b*) (*d*) (*f*)

Fig. S8. Partial density of states (PDOS) of H atoms both in 12 isolated H_2 molecules (*a*) and in $B_{12}@Li_{20}Al_{12}$-$12H_2$ (*b*), Al atoms both in $B_{12}@Li_{20}Al_{12}$ (*c*) and in $B_{12}@Li_{20}Al_{12}$-$12H_2$ (*d*) and Li atoms both in $B_{12}@Li_{20}Al_{12}$ (*e*) and in $B_{12}@Li_{20}Al_{12}$-$12H_2$ (*f*). The black dotted line is the Fermi level.



(*a*) (*b*)

Fig. S9. The statistical results of distances of H_2 molecules to the cluster of the $B_{12}@Li_{20}Al_{12}$ with 58 H_2 (two layers of absorbed H_2 molecules) absorbed for part (*a*) and 12 H_2 (the first layer of absorbed H_2 molecules) absorbed for part (*b*). We take the distance of 7.14 Å as the farthest distance of the absorbed H_2 molecules to the cluster center. We also listed the numbers of absorbed H_2 molecules at different temperatures during molecular dynamics simulations.

Table S1. The average distance of all types of connections between different atoms for the $B_{12}@Li_{20}Al_{12}$.

Average distance (Å)								
d_{B-B}	d_{B-Al}	d_{B-Li^I}	$d_{B-Li^{II}}$	d_{Al-Al}	d_{Li-Li}	d_{Al-Li^I}	$d^1_{Al-Li^{II}}$	$d^2_{Al-Li^{II}}$
1.88	2.46	2.45	2.47	2.63	2.60	2.58	2.60	2.58

Table S2. The charge partitioning of the core-shell $B_{12}@Li_{20}Al_{12}$ by Hirshfeld analysis.

Charge partitioning (e)			
B	Al	Li^I	Li^{II}
-0.08	-0.06	0.01	0.14

Table S3. The average adsorption energy (E_b) of per metal atom for the $B_{12}@Li_{20}Al_{12}$ and $B_{80}M_{12}$ (M= Li, Na, Mg, K, Ca and Sc).

Molecule	$B_{12}@Li_{20}Al_{12}$	$B_{80}Li_{12}$	$B_{80}Na_{12}$	$B_{80}Mg_{12}$	$B_{80}K_{12}$	$B_{80}Ca_{12}$	$B_{80}Sc_{12}$
E_b (eV)	2.78	2.77	1.77	1.33	1.70	2.31	4.06

Table S4. The distance of H_2 to the nearest metal atoms (d_{H-M}), adsorption energies (E_{ad}) and the desorption temperature (T_d) of H_2 molecule on the eleven specific adsorption locations. The specific meanings for the symbols of eleven specific adsorption locations have already been explained in Fig. S6.

Adsorption locations	T_1	T_2	T_3	B_1	B_2	B_3	B_4	B_5	C_1	C_2	C_3
d_{H-M} (Å)	1.95	3.04	3.71	-	-	-	-	-	-	-	-
E_{ad} (eV)	-0.32	-0.11	-0.12	-0.13	-0.13	-0.14	-0.13	-0.14	-0.14	-0.16	-0.16
T_d (K)	408	140	153	166	166	179	166	179	179	204	204

Table S5. The specific coordinates of every atom for the $B_{12}@Li_{20}Al_{12}$.

Atom	Coordinates (Å)		
	X	Y	Z
B	-0.155	-0.226	1.771
B	-1.657	-0.192	0.657
B	1.189	0.855	1.033
B	0.462	1.633	-0.577
B	-1.189	-0.856	-1.034
B	0.154	0.226	-1.772
B	-0.463	-1.634	0.576
B	-0.603	1.399	0.946
B	0.603	-1.399	-0.947
B	1.657	0.191	-0.659
B	-1.292	0.994	-0.751
B	1.292	-0.995	0.750
Li	-0.365	-1.718	-3.169
Li	0.361	1.718	3.174
Li	-1.208	3.408	-0.322
Li	-3.503	-0.044	-0.955
Li	1.926	1.733	-2.543
Li	3.505	0.038	0.958
Li	1.213	-3.416	0.326
Li	-1.938	-1.737	2.550
Li	2.817	2.081	2.419
Li	-0.309	-0.560	4.211
Li	0.314	0.569	-4.210
Li	3.037	-2.351	1.843
Li	-1.488	3.287	2.266
Li	1.487	-3.291	-2.263
Li	3.939	0.393	-1.582
Li	-3.035	2.364	-1.840
Li	-2.821	-2.092	-2.420
Li	1.152	3.887	-1.326
Li	-1.150	-3.890	1.322
Li	-3.941	-0.391	1.589
Al	2.030	-0.818	-2.879
Al	-2.033	0.816	2.879
Al	0.865	3.302	1.205
Al	0.547	-2.443	2.615
Al	-0.864	-3.304	-1.202
Al	-1.986	0.280	-3.016
Al	-0.548	2.445	-2.617
Al	1.982	-0.277	3.020
Al	-2.834	-2.253	0.187

Al	2.833	2.254	-0.186
Al	-3.025	1.880	0.691
Al	3.024	-1.881	-0.690