Supporting information for

$Ag@Mg_{12}@Ag_{20}$: A three-layer Matryoshka structure with S_6 symmetry

Peng-Bo Liu,[a] Jing-Jing Guo,[a] Yi-Sha Chen,[a] Hui-Yan Zhao,*[,a] Jing Wang,[a] and Ying Liu*[,a]

[1]*Department of Physics and Hebei Advanced Thin Film Laboratory, Hebei Normal University, Shijiazhuang 050024, Hebei, China*.

[2]*State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China.*

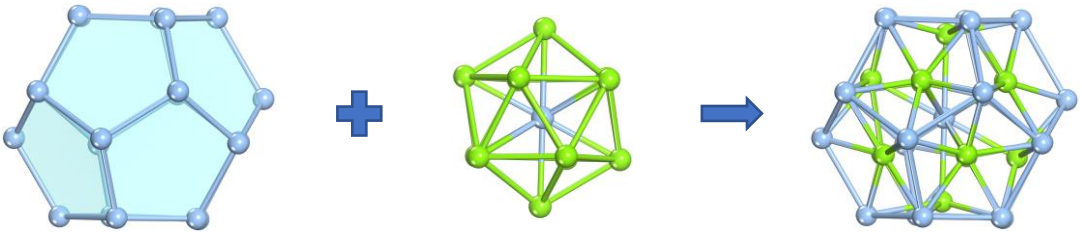


Figure S1. Detailed construction of core-shell $Ag@Mg_{12}@Ag_{20}$. The three-layer core-shell $Ag@Mg_{12}@Ag_{20}$ structure is formed by encapsulating an $Ag@Mg_{12}$ icosahedron within the Ag_{20} dodecahedron.

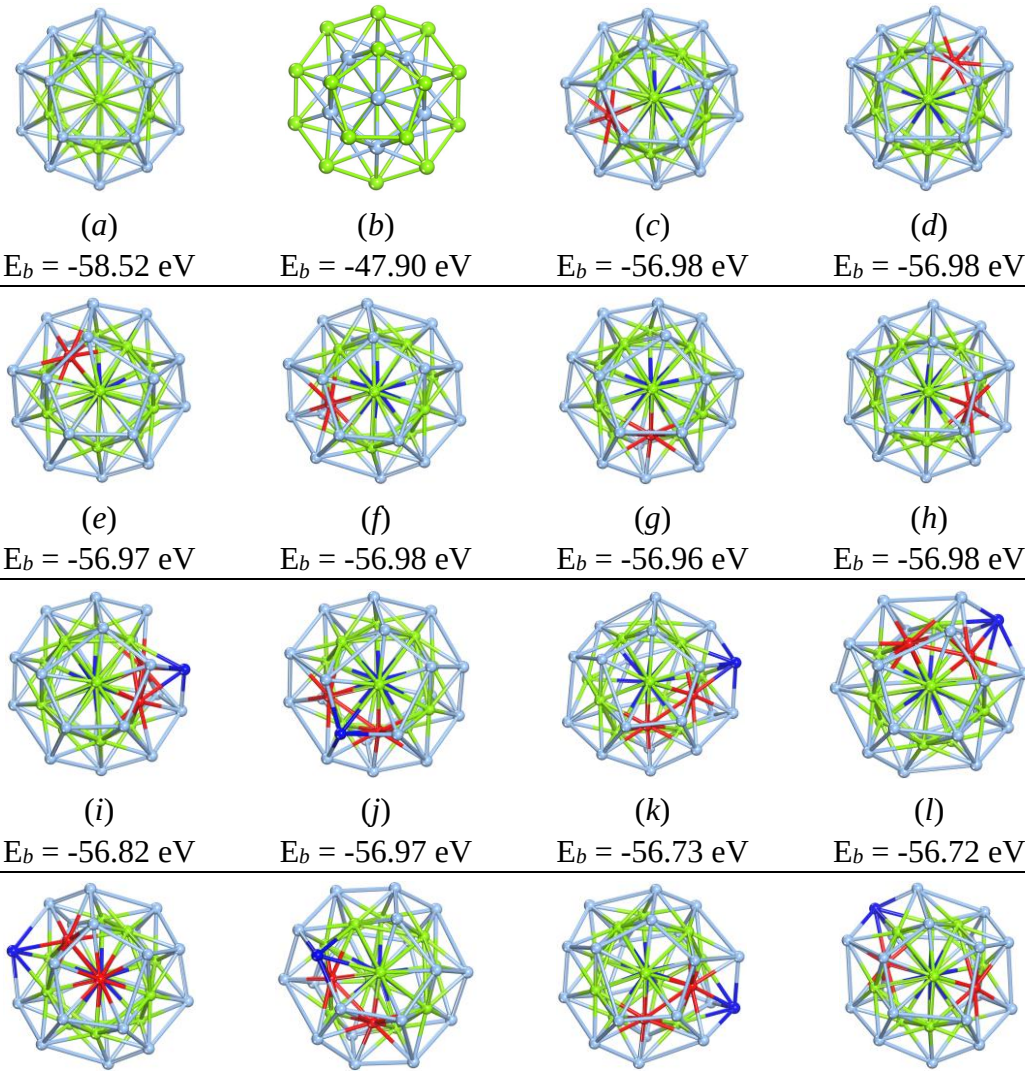
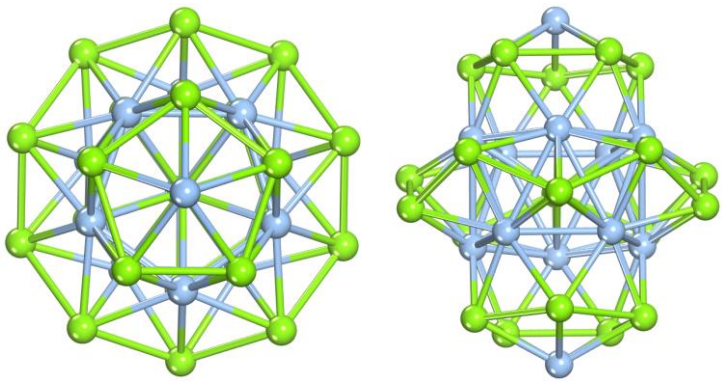


Figure S2. The proposed ideal $Ag@Mg_{12}@Ag_{20}$ structure for part (*a*), and fifteen structures obtained by swaps of Ag-Mg pairs for part (*b*-*p*) with the binding energies (E_b) listed below each configurations after energy minimizing. Part (*b*) shows the configuration of $Mg@Ag_{12}@Mg_{20}$ obtained by conducting complete swap of Ag-Mg pairs; part (*c*-*h*) show the configurations of $Mg@AgMg_{11}@Ag_{20}$ and part (*i*-*p*) show the configurations of $Mg@Ag_2Mg_{10}@MgAg_{19}$, the swapped Mg and Ag atoms are colored in blue and red, respectively.



(*a*) (*b*)

Figure S3. Top view (*a*) and side view (*b*) of the optimized $Mg@Ag_{12}@Mg_{20}$, which is obtained by conducting complete swap of Ag-Mg pairs in $Ag@Mg_{12}@Ag_{20}$.

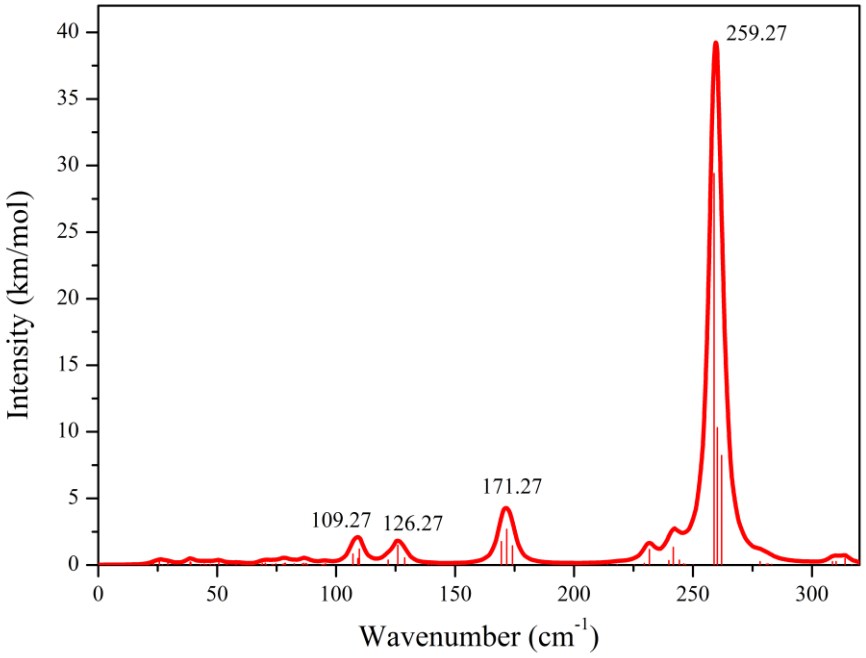
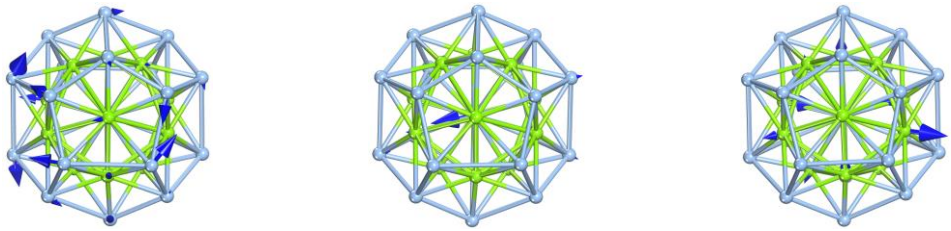


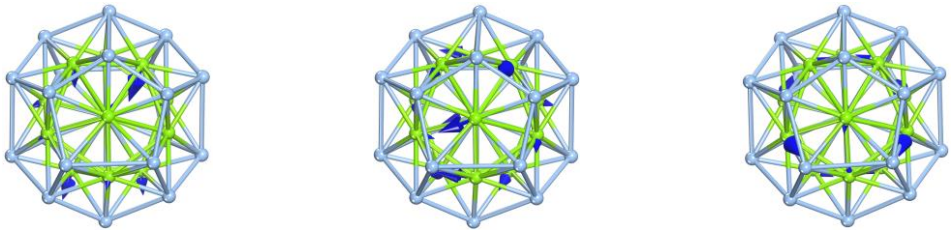
Figure S4. IR spectrum for the three-layer core-shell $Ag@Mg_{12}@Ag_{20}$.



Mode 01: f = 23.27 cm^{-1} Intensity = 0.07 km/mol

Mode 02: f = 109.27 cm^{-1} Intensity = 2.21 km/mol

Mode 03: f = 126.27 cm^{-1} Intensity = 1.91 km/mol

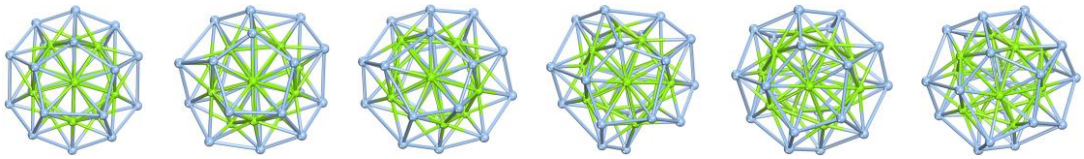


Mode 04: f = 171.27 cm^{-1} Intensity = 4.44 km/mol

Mode 05: f = 259.27 cm^{-1} Intensity = 41.41 km/mol

Mode 06: f = 319.66 cm^{-1} Intensity = 0.02 km/mol

Figure S5. The lowest frequency mode (Mode 01) and the highest frequency mode (Mode 06) of the three-layer core-shell $Ag@Mg_{12}@Ag_{20}$ are depicted. Additionally, several frequency modes exhibiting higher mode intensities are listed for reference.



0 *ps* 2 *ps* 4 *ps* 6 *ps* 8 *ps* 10 *ps*

Figure S6. *Ab into* molecular dynamics simulations for the three-layer $Ag@Mg_{12}@Ag_{20}$ structure at 500 K, insets depicting snapshots at 0 *ps*, 2 *ps*, 4 *ps*, 6 *ps*, 8 *ps*, 10 *ps*.

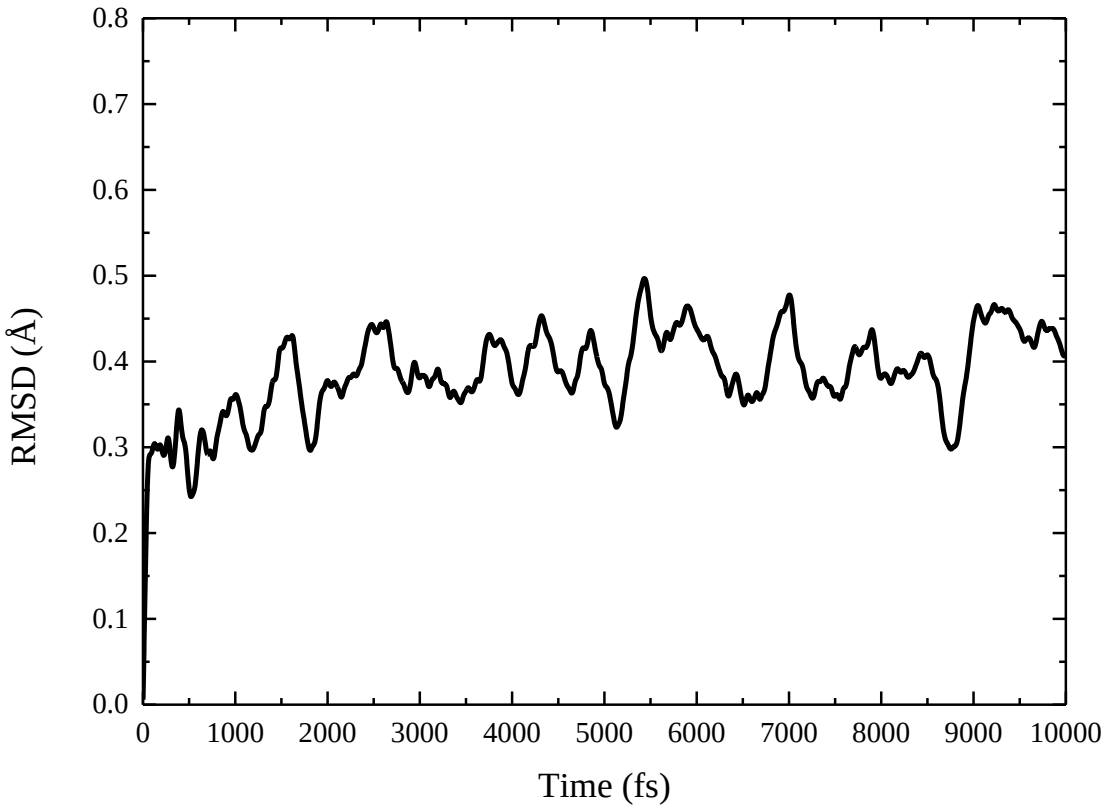
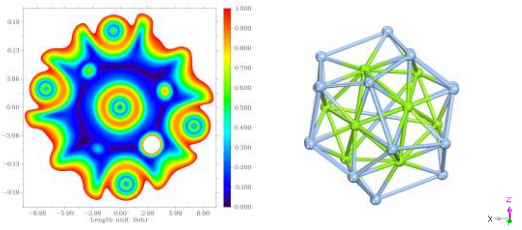
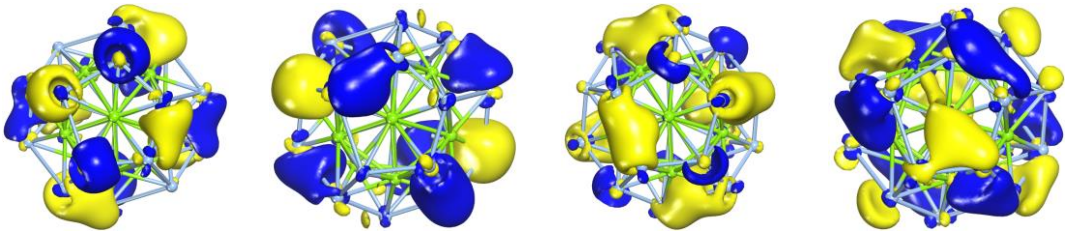


Figure S7 Coordinate root-mean-square deviation (RMSD) based on the molecular dynamics (MD) simulations at 500 *K* for the three-layer Ag@Mg_{12}@Ag_{20} structure. This plot illustrates the RMSD values over time, emphasizing the structural stability and deviations observed throughout the simulations.



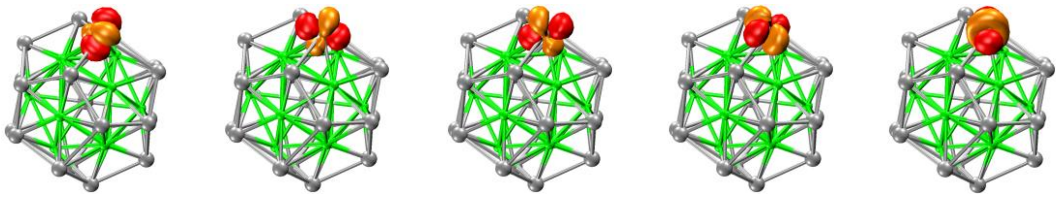
(*a*) (*b*)

Figure S8. The reduced density gradient (RDG) for Ag@Mg_{12}@Ag_{20} sections along the XZ plane with the different values of RDG colored from dark blue to red for part (*a*), the corresponding view of Ag@Mg_{12}@Ag_{20} structure for part (*b*).



HOMO-2 HOMO LUMO LUMO+3

Figure S9. Selected representative frontier molecular orbitals for the three-layer core-shell $Ag@Mg_{12}@Ag_{20}$ structure with the isosurface value of 0.02 e/Å^3.



(*a*) (*b*) (*c*) (*d*) (*e*)

Figure S10. Five *d*-type lone pairs on one Ag atom in the Ag_{20} dodecahedron.

Table S1. Natural population charge analysis (NPA) for the three-layer core-shell $Ag@Mg_{12}@Ag_{20}$ structure.

Number	Atom	Charge	Number	Atom	Charge	Number	Atom	Charge
1	Mg	-0.48	12	Mg	-0.46	23	Ag	0.36
2	Mg	-0.47	13	Ag	-0.72	24	Ag	0.36
3	Mg	-0.51	14	Ag	0.21	25	Ag	0.27
4	Mg	-0.49	15	Ag	0.39	26	Ag	0.27
5	Mg	-0.49	16	Ag	0.26	27	Ag	0.36
6	Mg	-0.51	17	Ag	0.39	28	Ag	0.36
7	Mg	-0.51	18	Ag	0.39	29	Ag	0.38
8	Mg	-0.51	19	Ag	0.21	30	Ag	0.39
9	Mg	-0.48	20	Ag	0.39	31	Ag	0.36
10	Mg	-0.48	21	Ag	0.39	32	Ag	0.27
11	Mg	-0.46	22	Ag	0.27	33	Ag	0.27