# Electronic Supplementary Information

## Effects of Subnanometer Silver Clusters on Photocatalyst AgBr(110) Surface: A Theoretical Investigation

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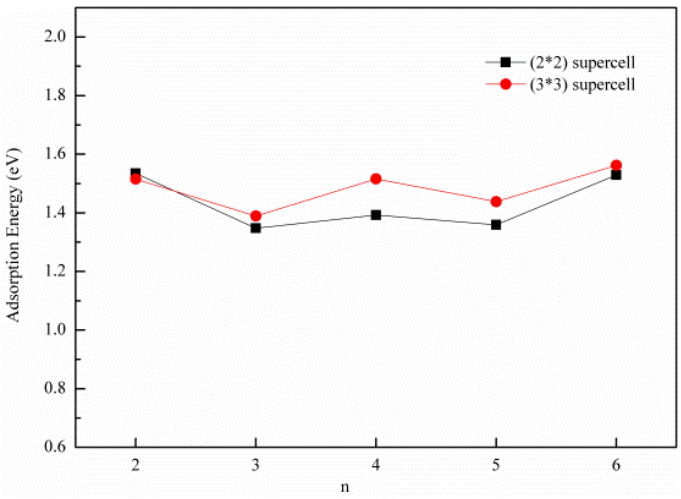


**Fig. S1.** The adsorption energies of $Ag_n$ on the AgBr(110) supercells of (2 × 2) (black) and (3 × 3) (red).

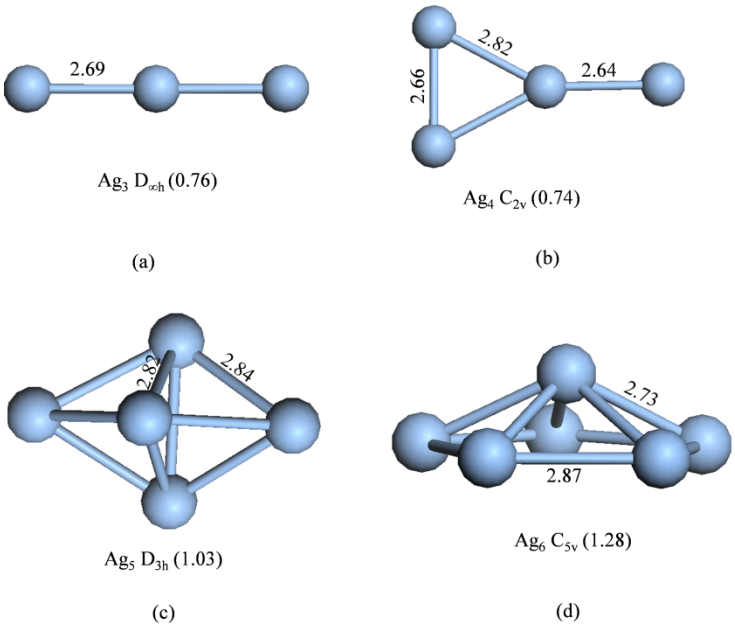


**Fig. S2.** The second most stable structures of clusters $Ag_n$ (n = 3 – 6) with the bond lengths in Å. Given below are the symmetry groups together with the binding energies in eV.

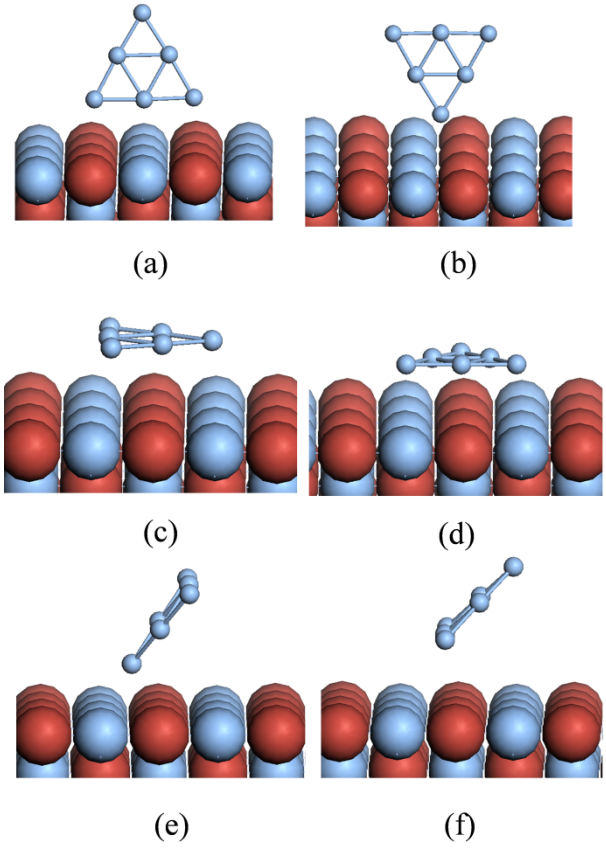


**Fig. S3.** The adsorption mode for the most stable $Ag_n$ cluster on the AgBr(110) surface. (a) and (b) vertical; (c) and (d) horizontal; (e) and (f) inclined.

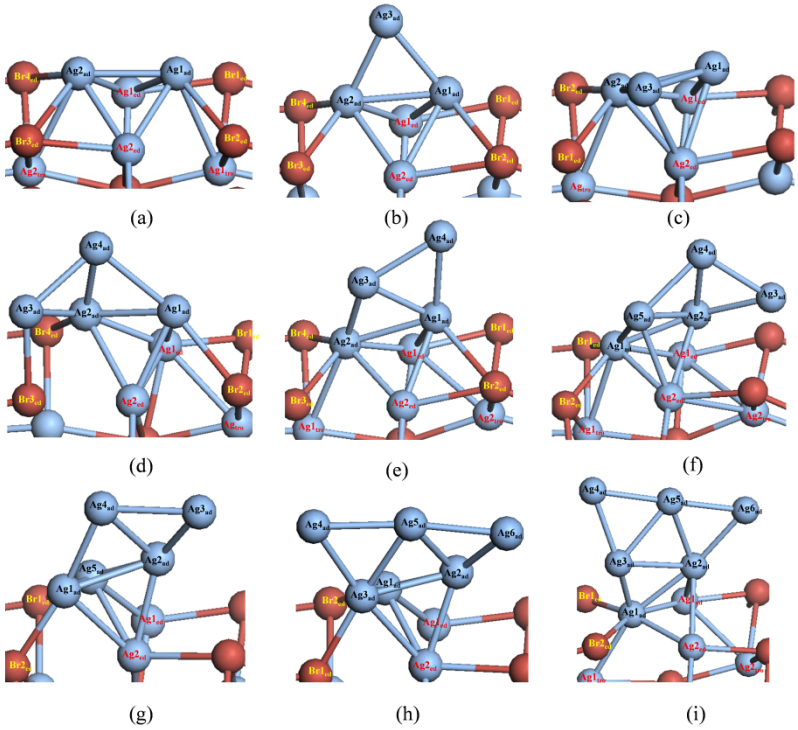


**Fig. S4.** The second most and third most stable structures of $Ag_n$/AgBr(110). (a) $Ag_2$/AgBr(110); (b) and (c) $Ag_3$/AgBr(110); (d) and (e) $Ag_4$/AgBr(110); (f) and (g) $Ag_5$/AgBr(110); (h) and (i) $Ag_6$/AgBr(110). Only two stable structures are found for $Ag_2$ on the AgBr(110) surface. Silver and bromine atoms are indicated as light blue and wine spheres.

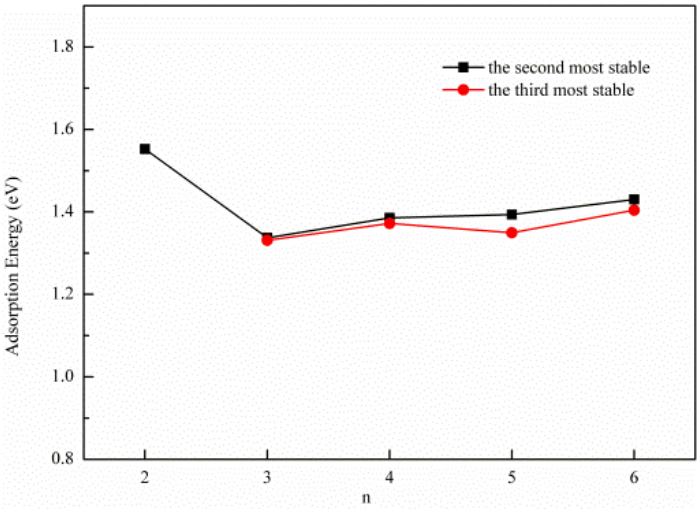


**Fig. S5.** Adsorption energies for the second most and third most stable structures of $Ag_n$/AgBr(110).

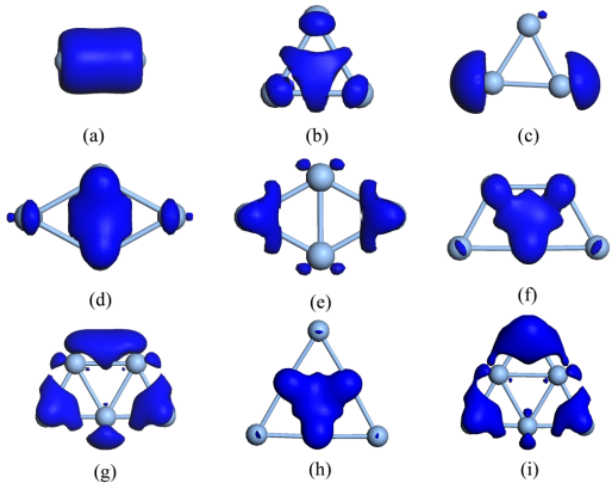


**Fig. S6.** The isosurface plots of wave functions for the free clusters. (a) at the Fermi level of $Ag_2$; (b) and (c) below and at the Fermi level of $Ag_3$; (d) and (e) below and at the Fermi level of $Ag_4$; (f) and (g) below and at the Fermi level of $Ag_5$; (h) and (i) below and at the Fermi level of $Ag_6$. Isovalue considered is 0.02 electron/Å$^3$.

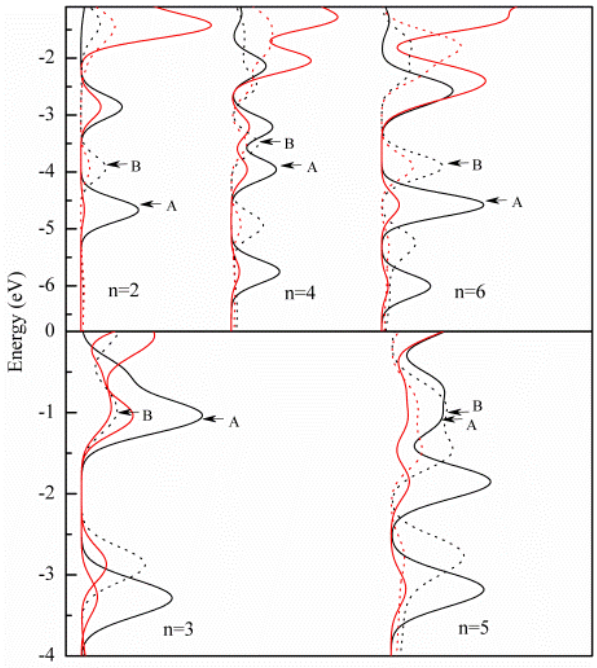


**Fig. S7.** Partial density of states (PDOSs) of the Ag 5s/5p states of $Ag_n$ near the Fermi level. A and B represent the Fermi level of the free and adsorbed systems. Solid and dot lines denote free and adsorbed clusters; red and black lines denote Ag 5s and 5p states.

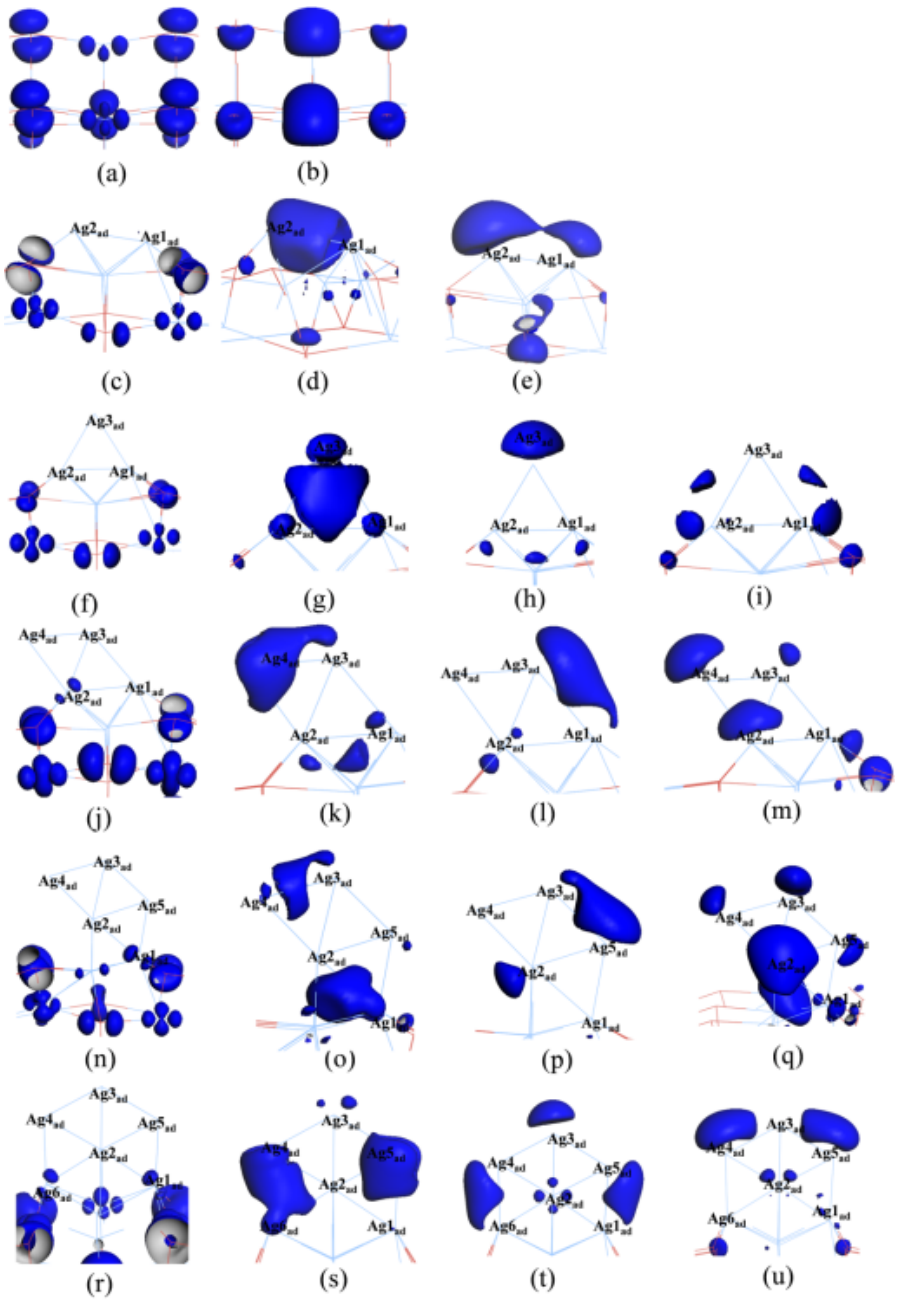


**Fig. S8.** The isosurface plots of wave functions for the clean and adsorbed AgBr(110) surfaces. (a) and (b) VBM and CBM of the clean surface; (c), (d) and (e) VB, MIGB and CB of $Ag_2$/AgBr(110); (f), (g) and (h,i) VB, MIGB and CB of $Ag_3$/AgBr(110); (j), (k) and (l, m) VB, MIGB and CB of $Ag_4$/AgBr(110); (n), (o, p) and (q) VB, MIGB and CB of $Ag_5$/AgBr(110); (r), (s) and (t, u) VB, MIGB and CB of $Ag_6$/AgBr(110). Isovalue is 0.02 electron/Å$^3$ for the VB and 0.016 electron/Å$^3$ for the MIGB and CB.

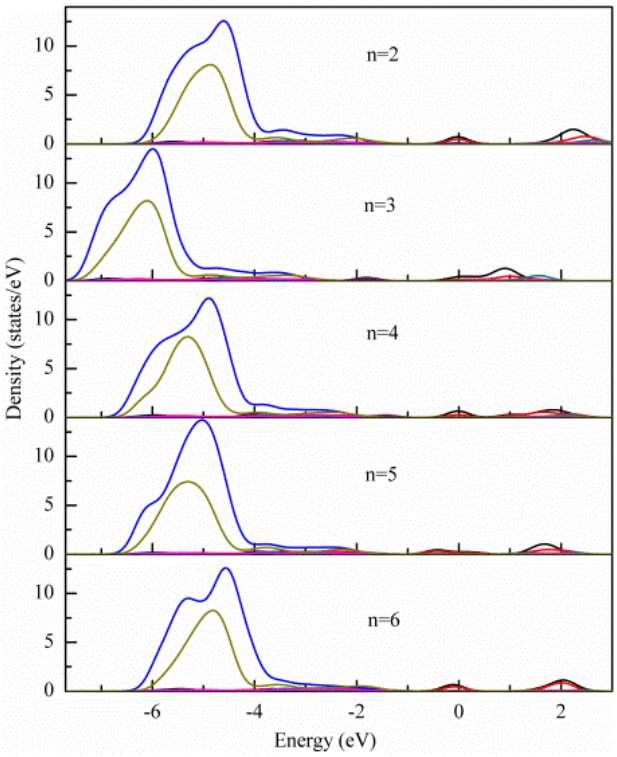


**Fig. S9.** The PDOS of $Ag_{ed}$ and $Ag_{tro}$ on the $Ag_n$/AgBr(110) surfaces. Black line is for $Ag_{ed}$ 5s, red line is for $Ag_{ed}$ 5p, blue line is for $Ag_{ed}$ 4d, dark cyan line is for $Ag_{tro}$ 5s, magenta line is for $Ag_{tro}$ 5p, dark yellow is for $Ag_{tro}$ 4d. The energy is referenced to the Fermi level of the $Ag_n$/AgBr system.

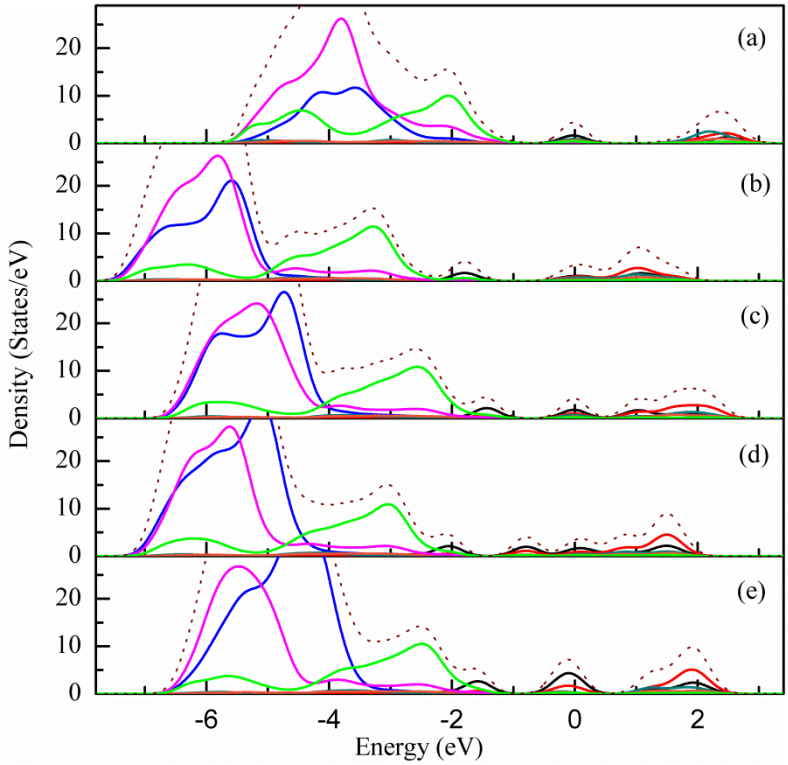


**Fig. S10.** Partial density of states (PDOSs) of cluster Ag 5s, 5p, 4d, surface Ag 5s, 5p, 4d and Br 4p states of the second most stable structures for (a) Ag2/AgBr(110), (b) Ag3/AgBr(110), (c) Ag4/AgBr(110), (d) Ag5/AgBr(110), (e) Ag6/AgBr(110). Black line is for Agad 5s, red line is for Agad 5p, blue line is for Agad 4d, dark cyan line is for Aged 5s, orange line is for Aged 5p, magenta line is for Aged 4d, green line is for Bred 4p, and wine dot line is the sum of the local DOS of all Ag and Br atoms in the first layer of the adsorbed system. The energy is referenced to the Fermi level of the Agn/AgBr system.

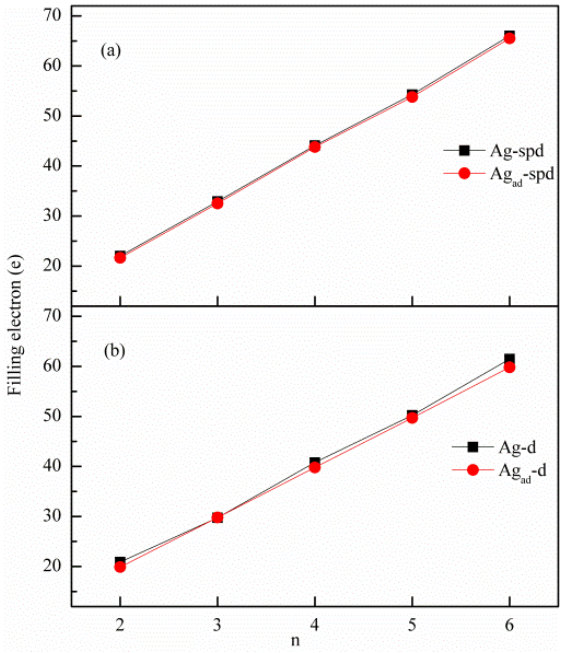


**Fig. S11.** The filling electron for free (black line) and adsorbed (red line) Ag clusters.

(a) spd filling electrons; (b) d filling electrons.

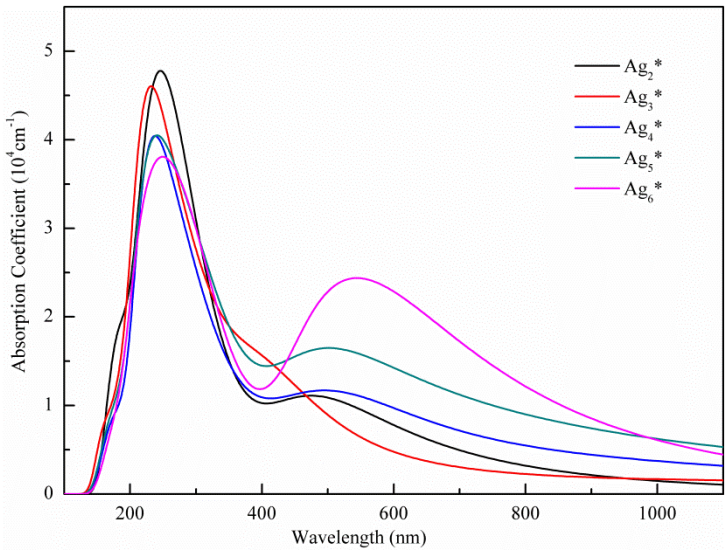


Fig. S12. The calculated optical absorption coefficients for the second most stable structures of $Ag_n$/AgBr(110) surfaces.

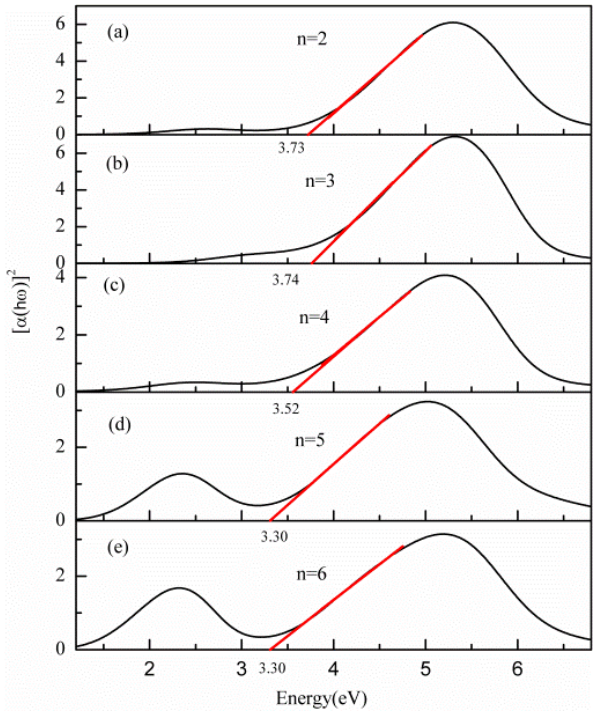


**Fig. S13.** The band gap estimation for the $Ag_n$/AgBr(110) systems.

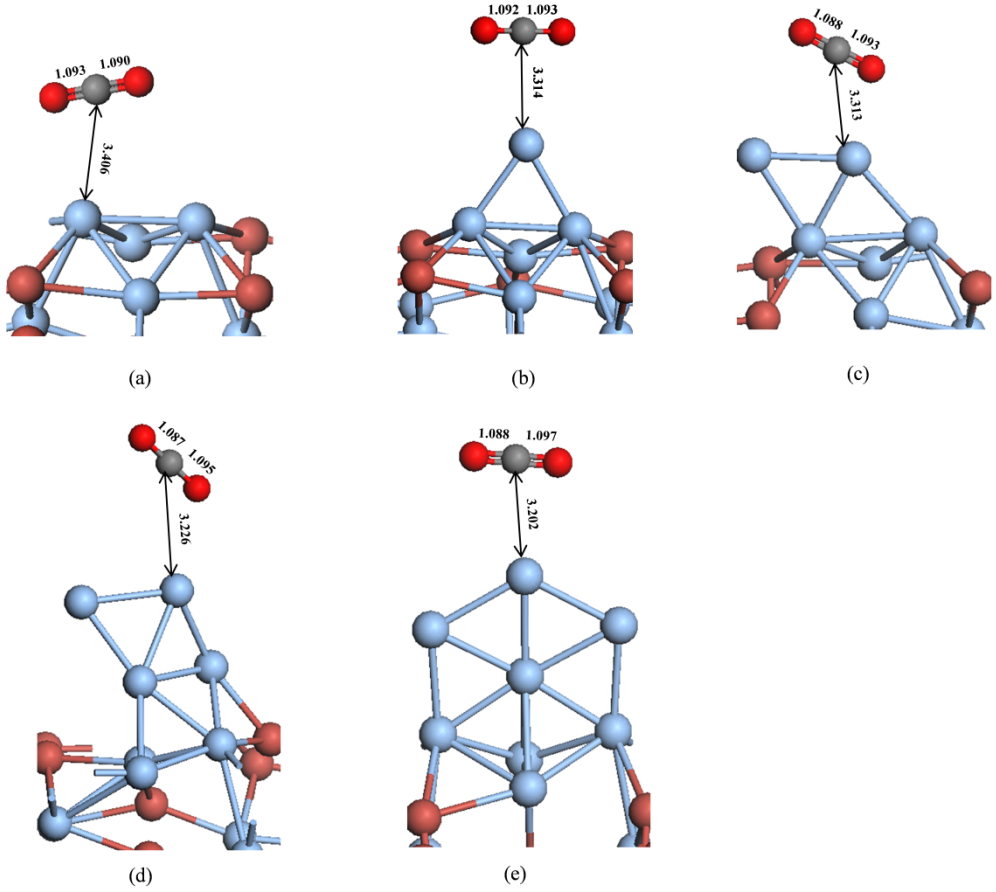


**Fig. S14.** The adsorption structures of $CO_2$ on the $Ag_n$/AgBr(110) (n = 2 - 6) surfaces. Given on figures are the C-O bond length and the distance in Å.

**Table S1.** The d-band centers of the free and adsorbed silver clusters (in eV) as well as the shifts of the d-band centers (in eV) after adsorptions.

| Cluster | Free ($d_1$) | Adsorbed ($d_2$) | $\Delta d$ |
|---|---|---|---|
| $Ag_2$ | -7.93 | -8.34 | 0.41 |
| $Ag_3$ | -5.69 | -6.56 | 0.87 |
| $Ag_4$ | -7.70 | -8.22 | 0.52 |
| $Ag_5$ | -5.05 | -5.78 | 0.73 |
| $Ag_6$ | -7.65 | -8.01 | 0.36 |

**Section S1.** The Computational details of $CO_2$ adsorbed on the $Ag_n$/AgBr(110) surfaces:

The molecular $CO_2$ were adsorbed on the most stable structures of $Ag_n$/AgBr(110) (n = 2 - 6) surfaces. The initial structures were assumed by the linear $CO_2$ molecular always keeping at a distance of 3.0 Å from the top of the $Ag_n$ clusters on the substrate, similar to the adsorption mode of oxygen on the Pt clusters [1]. The stable adsorption configurations of $CO_2$/$Ag_n$/AgBr(110) were optimized in CASTEP, using the parameters as mentioned in manuscript. The adsorption energy was calculated by the following formula:

$$E_{ad} = -\left(E_{CO_2/Ag_n/AgBr} - E_{Ag_n/AgBr} - E_{CO_2}\right)$$

References

[1] T. Imaoka, H. Kitazawa, W. -J. Chun, S. Omura, K. Albrecht, and K. Yamamoto, J. Am. Chem. Soc. 2013, 135, 13089−13095.