Electronic Supplementary Information

Effects of Atomic Ag on Photocatalyst AgBr surfaces: A Theoretical Survey

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Table S1. The Hubbard *U* parameters (eV) for Ag(d) and Br(p) and the resulting band gap (eV) for bulk AgBr.

$U_{Ag,d}$	$U_{Br,p}$	Band gap
2.0	1.8	2.798
1.8	1.5	2.703
1.6	1.3	2.633
1.4	1.1	2.563

Table S2. The calculated Mulliken atomic populations for the bulk, clean and atomic Ag adsorbed (100) and (110) facets of AgBr.

Orbitals	Bulk	Clean (100)	Adsorbed (100)	Clean (110)	Adsorbed (110)
[a]Br s	1.68	1.91	1.73	1.96	1.92
[a]Br p	5.37	5.4	5.35	5.4	5.38
[a]Ag s	0.43	0.38	0.48	0.37	0.52
[a]Ag p	0.54	0.45	0.54	0.41	0.47
[a]Ag d	9.99	9.98	9.97	9.98	9.96
[b]Ag s			0.84		0.63
[b]Ag p			0.23		0.53
[b]Ag d			9.96		9.93

[a]Br/Ag represents Br/Ag_{sur} for the clean (100), Br/Ag_{1sur} for the adsorbed (100), Br/Ag_{ed} for the clean (110), and Br/Ag_{1ed} for the adsorbed (110) facet. [b]Ag represents the adsorbed Ag (Ag_{ad})

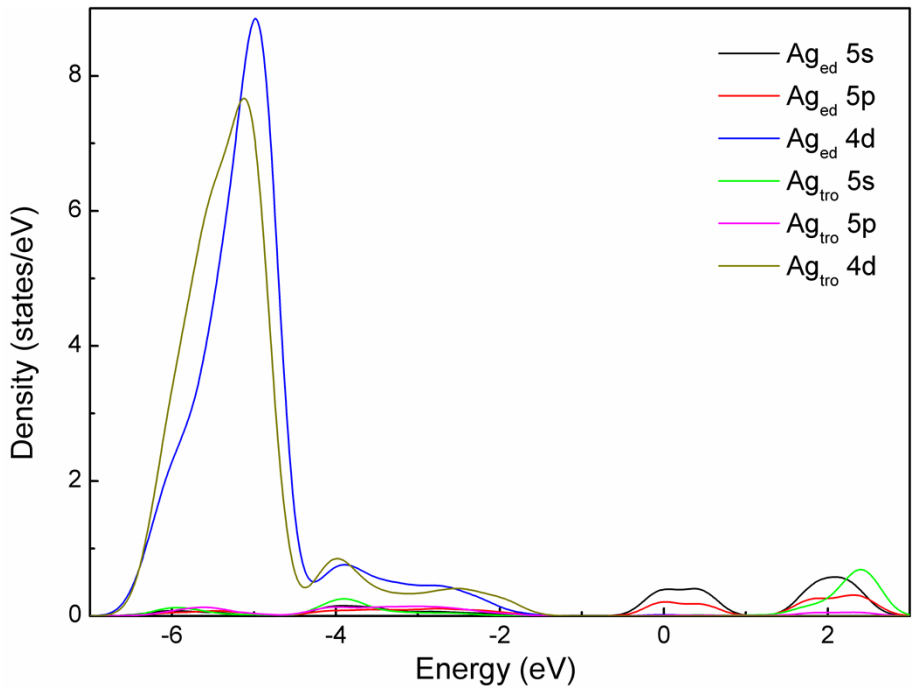

Fig. S1. The PDOS of Ag_{ed} and Ag_{tro} on the atomic Ag adsorbed AgBr(110) facet.

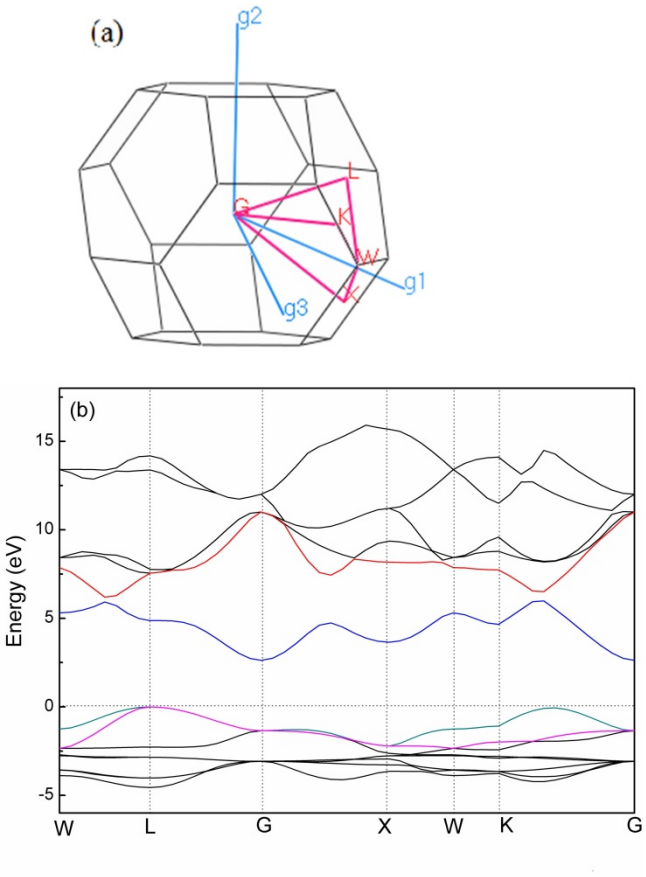

Fig. S2. Brillouin zone of bulk AgBr in reciprocal lattice (a). Band structure of bulk AgBr (b).

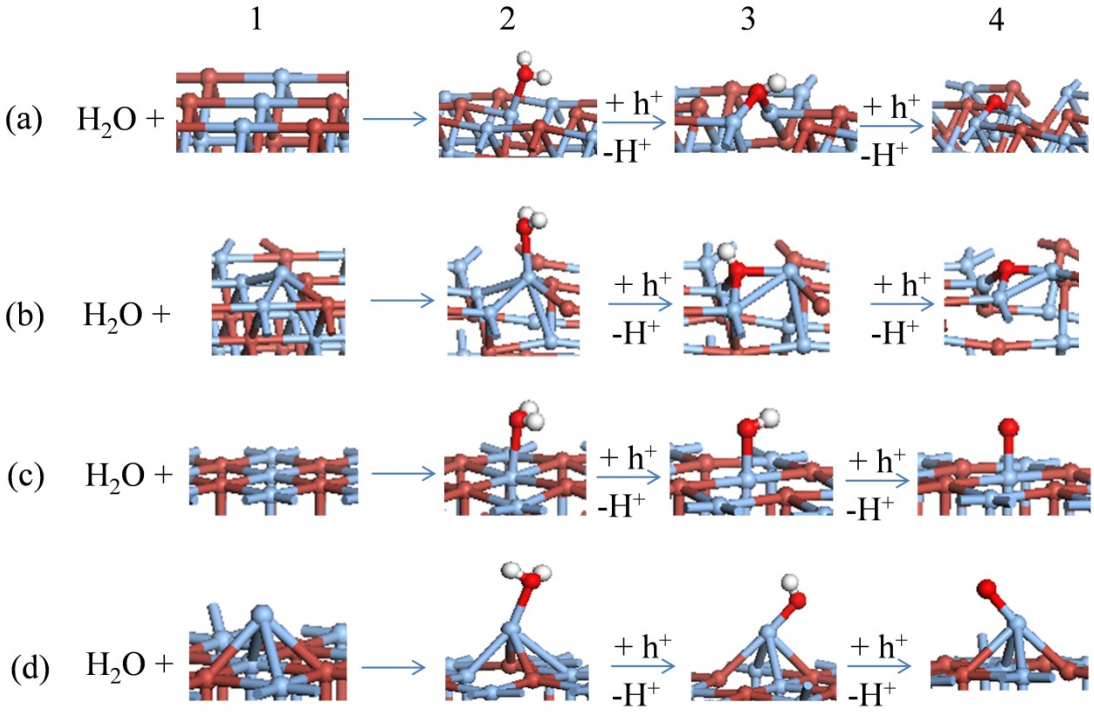

Fig. S3. Intermediate structures for water dissociation on the clean AgBr(110) (a), atomic Ag adsorbed AgBr(110) (b), clean AgBr(100) (c), and atomic Ag adsorbed Br(100) (d) facets.

Section S1. Estimation of the positions of the conduction band and the valence band

The position of the conduction band can be estimated using the equation[1]:

$$E_{CB} = X - E_C - 0.5E_g,$$

$$E_{VB} = E_g + E_{CB},$$

where E_C represents the energy of free electrons on the hydrogen scale (4.5 eV), X is the electronegativity of the semiconductor, and E_g represents the bandgap of the system.

The CBM of the bulk AgBr is calculated to be -3.42 eV (vs NHE), and the VBM to be -0.79eV (vs NHE). This VBM potential does not meet the hydrolysis to produce H_2, $\psi^0(H_2/H_2O) = 0\ eV$ (vs NHE). But the VBM is more positive than $\psi^0(O_2/H_2O) = -1.23\ eV$ (vs NHE), rendering water oxidization occur to generate O_2 with the help of the photogenerated holes over the AgBr.

References

[1] C. An, J. Wang, W. Jiang, M. Zhang, X. Ming, S. Wang and Q. Zhang, *Nanoscale* 2012, *4*, 5646.