

## Supporting Information

### The bandgap of sulfur-doped Ag<sub>2</sub>O nanoparticles

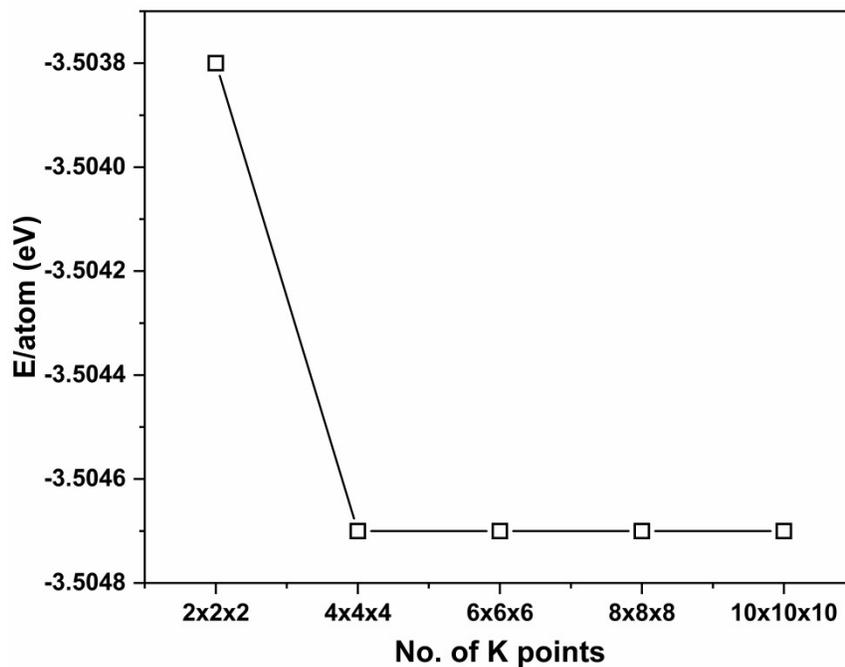
by

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**Fig. S1** K point optimization on Ag<sub>2</sub>O 2 × 2 × 2 supercell.

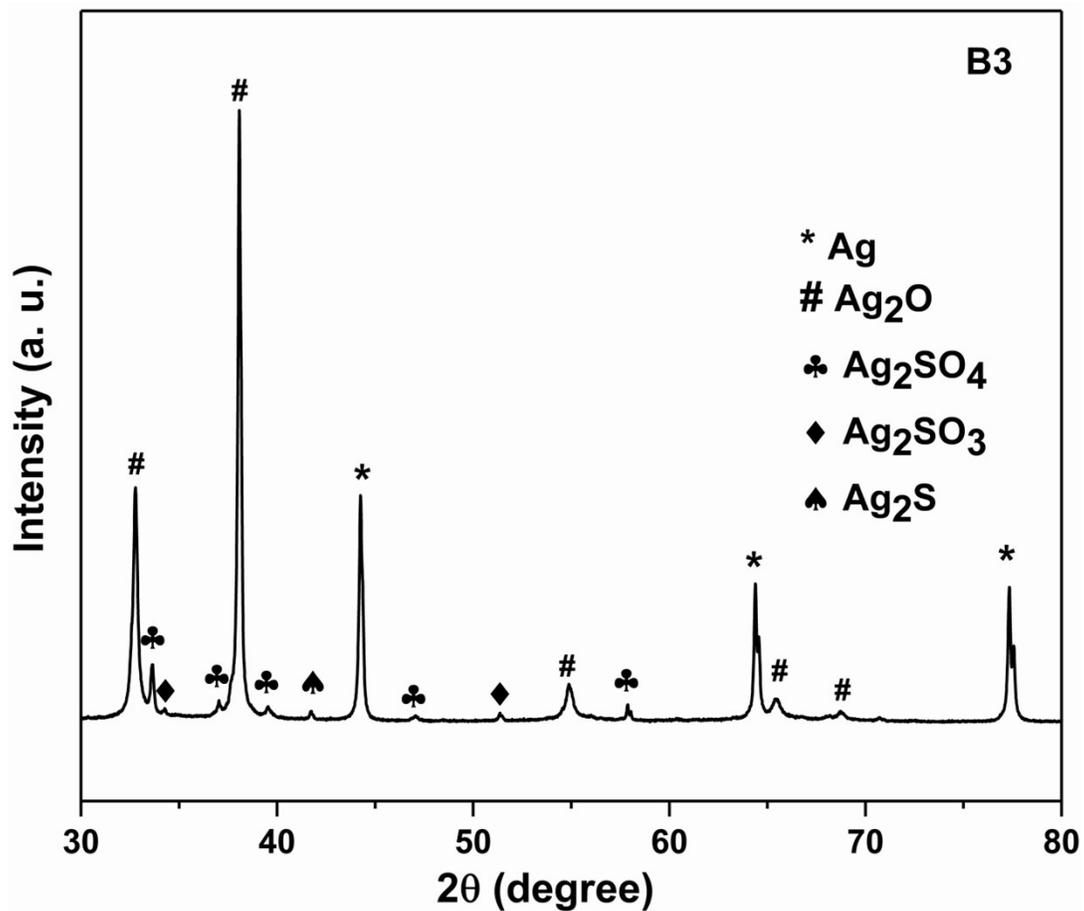
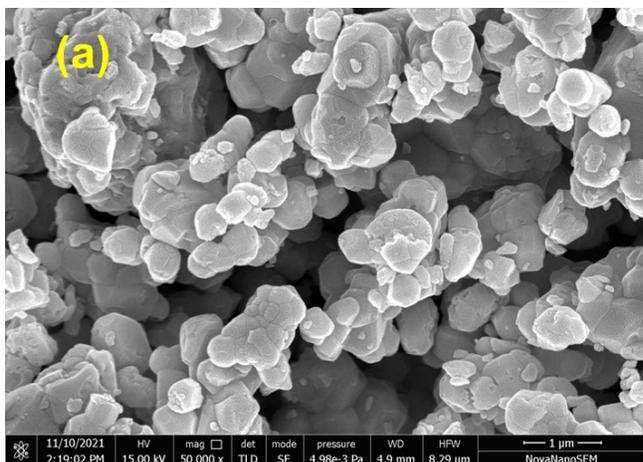
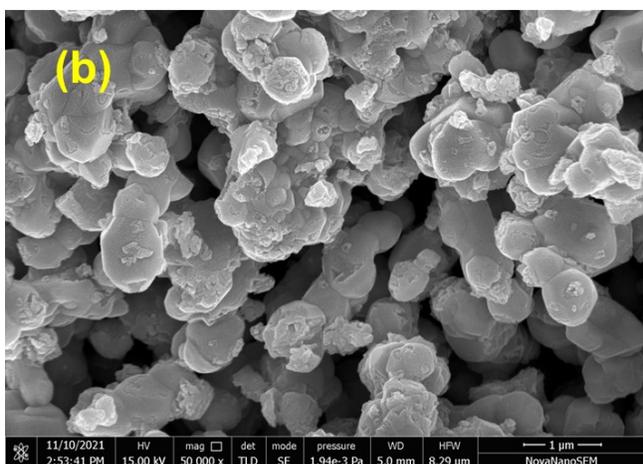


Fig. S2 Powder XRD pattern of B3 sample.



B1 sample		
Element	Weight %	Atomic %
O K	3.09	17.36
S K	0.95	2.67
AgL	95.96	79.97



B2 sample		
Element	Weight %	Atomic %
O K	2.48	14.23
S K	1.30	3.73
AgL	96.22	82.04

**Fig. S3** High resolution SEM micrograph of (a) B1 and (b) B2 samples.

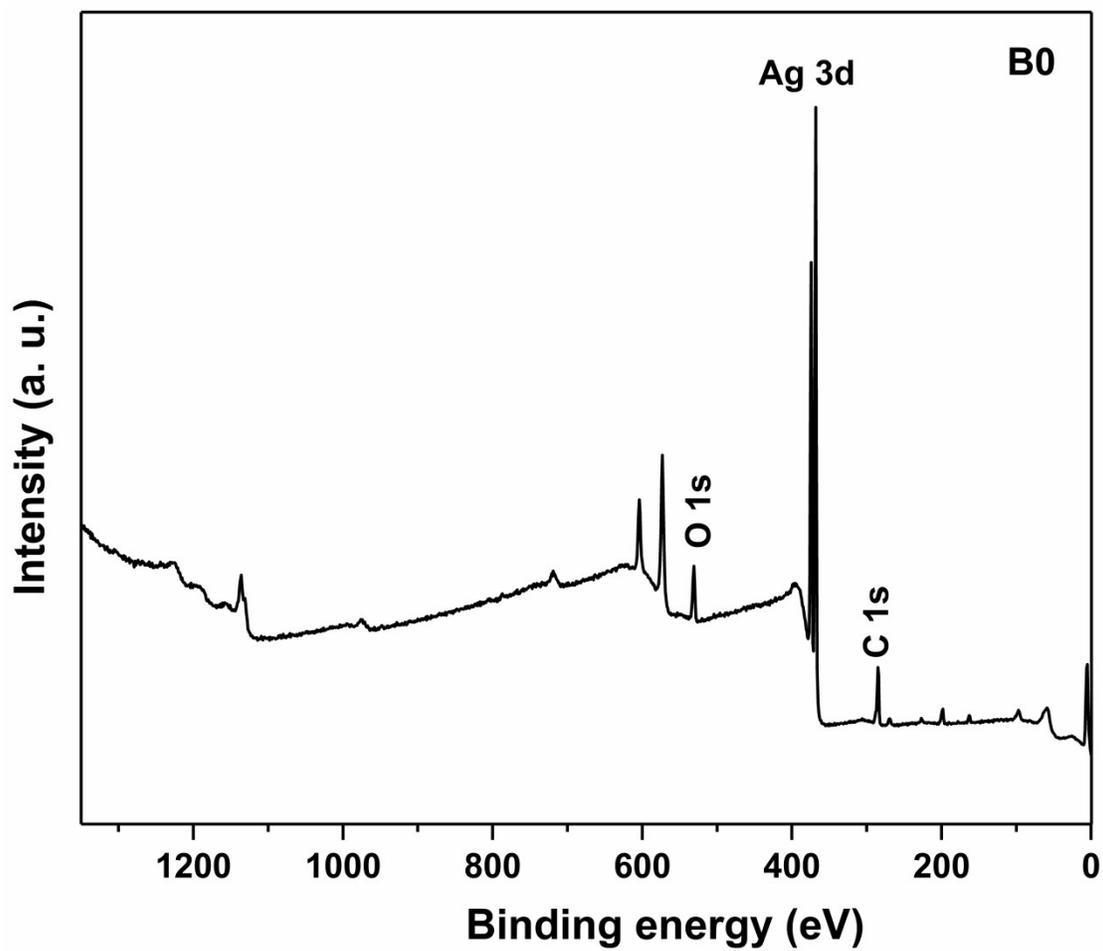


Fig. S4 XPS survey spectrum of B0 sample.

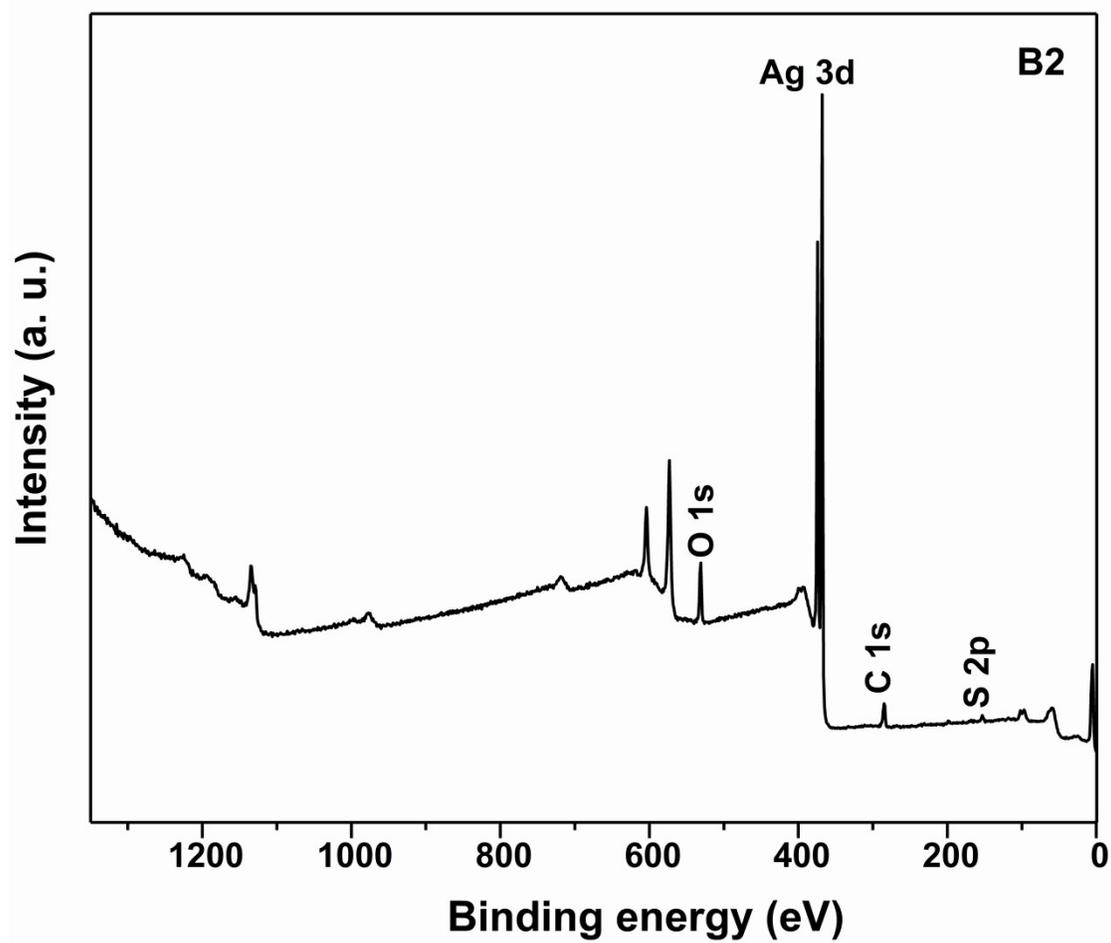
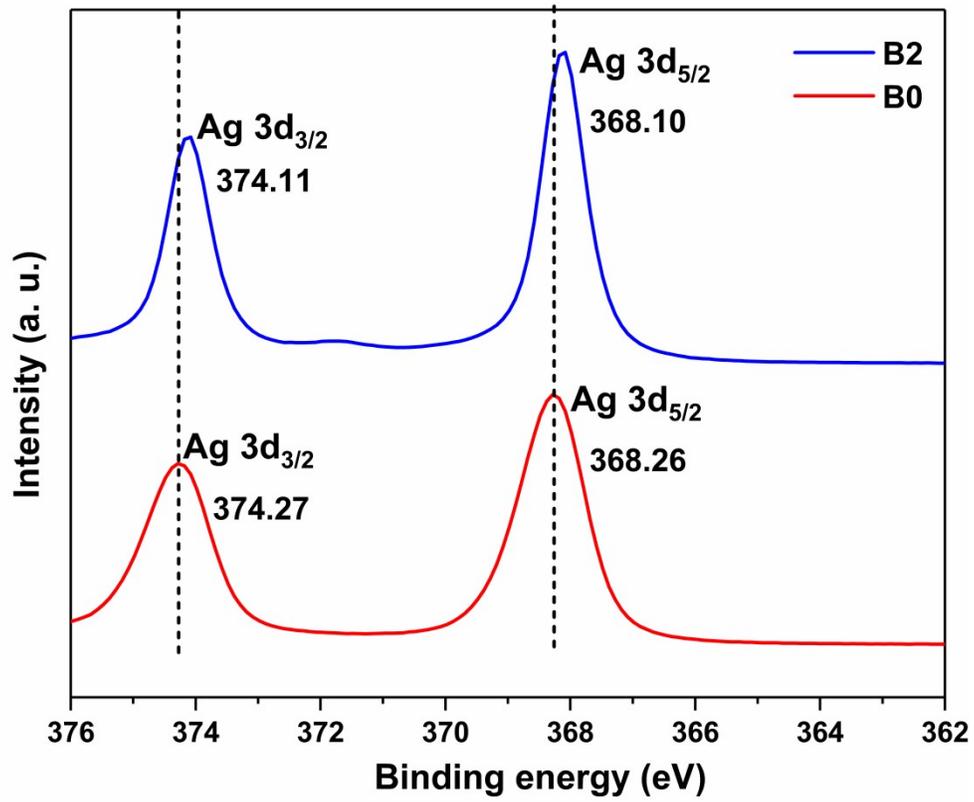
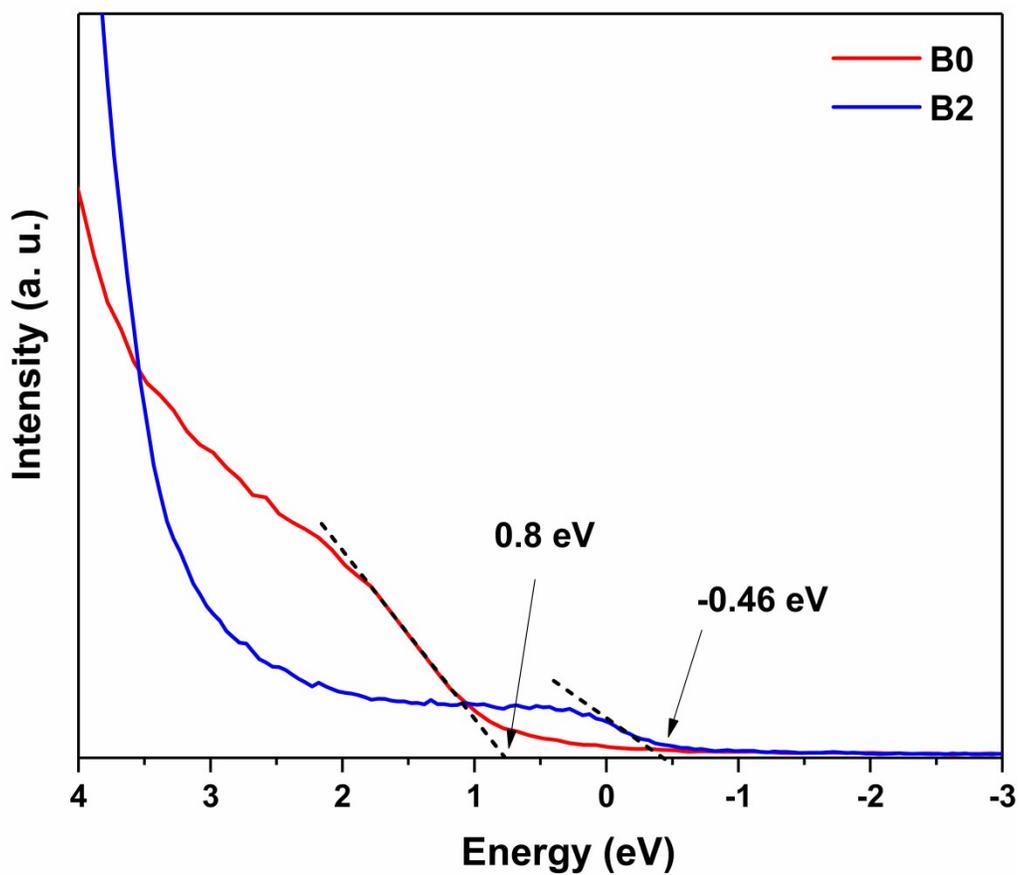


Fig. S5 XPS survey spectrum of B2 sample.



**Fig. S6** Comparison of high resolution XPS spectrum of Ag 3d for undoped (B0) and doped (B2) Ag<sub>2</sub>O.



**Fig. S7** Valence band XPS spectrum of B0 and B2 samples.

**Table S1** The position of VB and CB for the undoped and doped samples

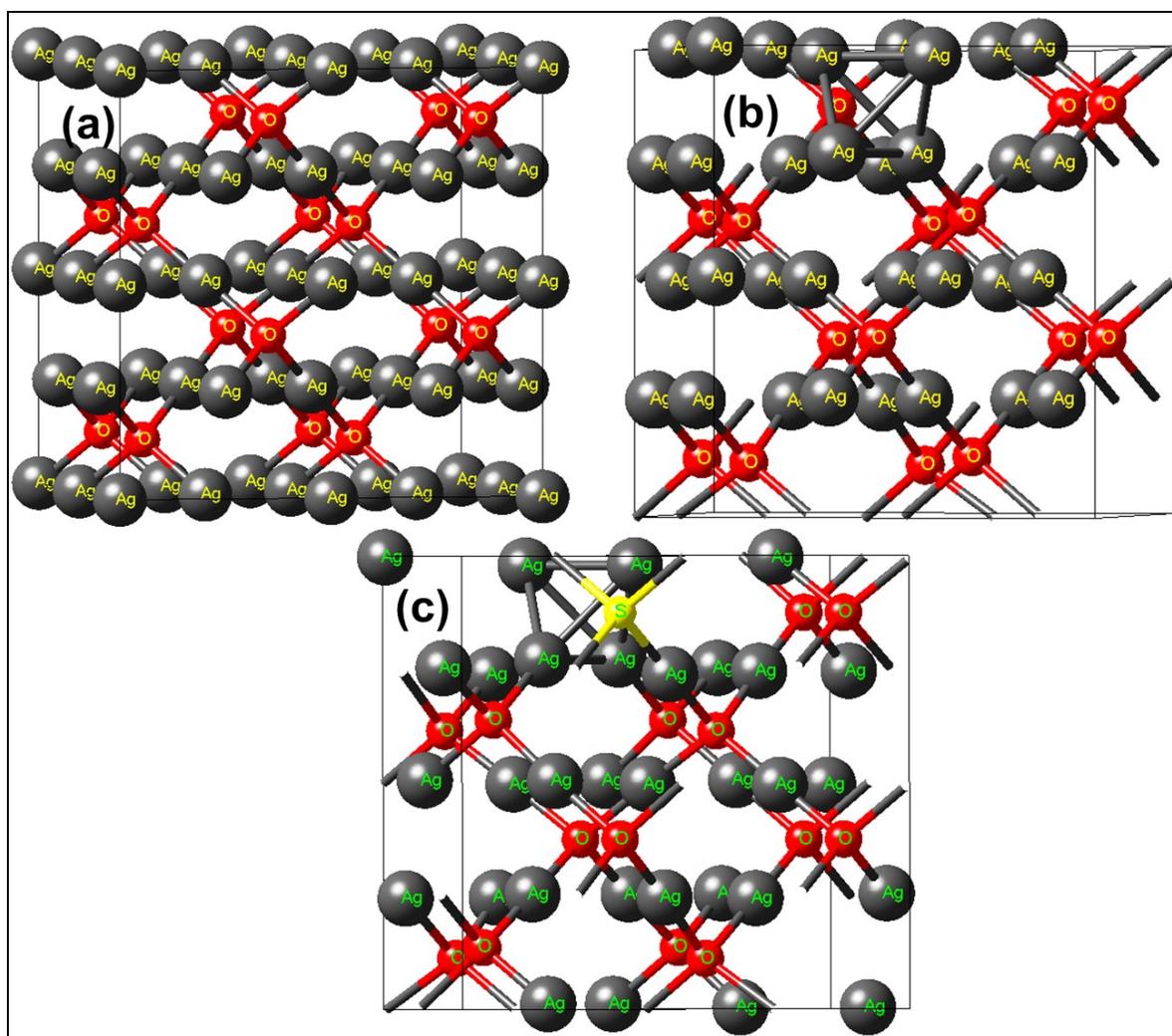
Samples	VB (eV)	CB (eV)
B0	0.80	-0.73
B1	-0.48	-2.18
B2	-0.46	-2.35

**Table S2** The formation energies and bandgap values of all the models attempted from DFT analysis.

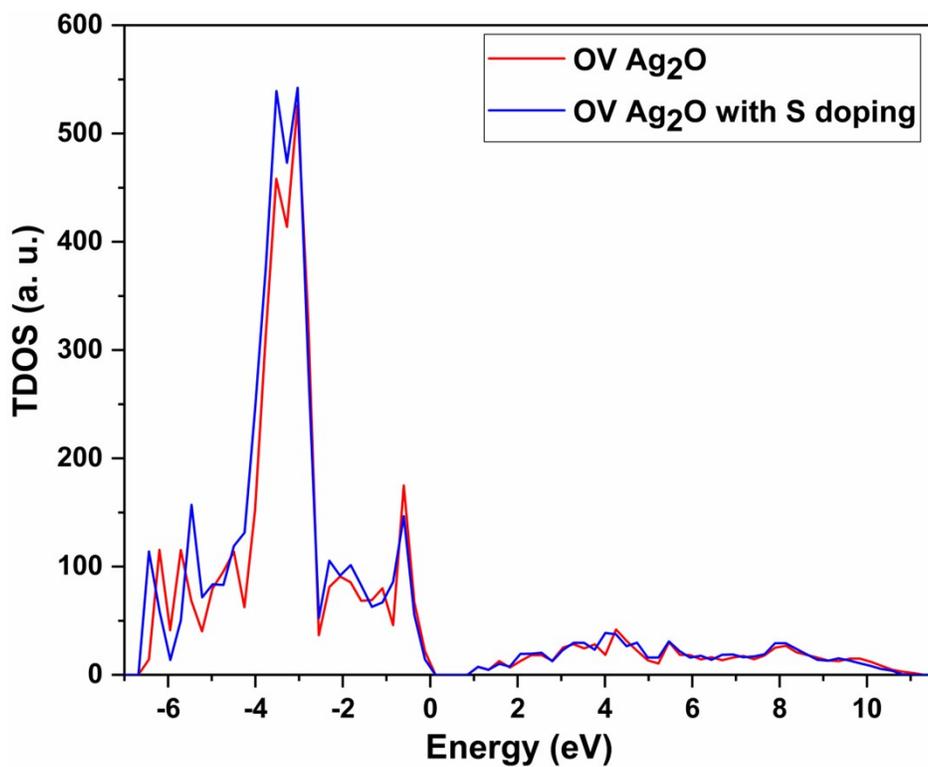
<b>Model</b>	<b>Formation energy (eV)</b>	<b>Bandgap (eV)</b>
<b>C0</b>	-	0.52
<b>CP1</b>	0.71	0.60
<b>CP2</b>	1.97	0.06
<b>C1</b>	1.29	1.05
<b>C2</b>	1.17	1.09
<b>C3</b>	1.54	0.28
<b>C4</b>	2.89	1.04

**Table S3** Calculation of energy per atom with the supercell size of the sulfur doped-Ag<sub>2</sub>O.

<b>Supercell</b>	<b>No. of atoms</b>	<b>Energy per atom (E/atom) (eV)</b>
2 × 2 × 2	47	-3.50
4 × 2 × 2	94	-3.50
4 × 4 × 2	188	-3.50



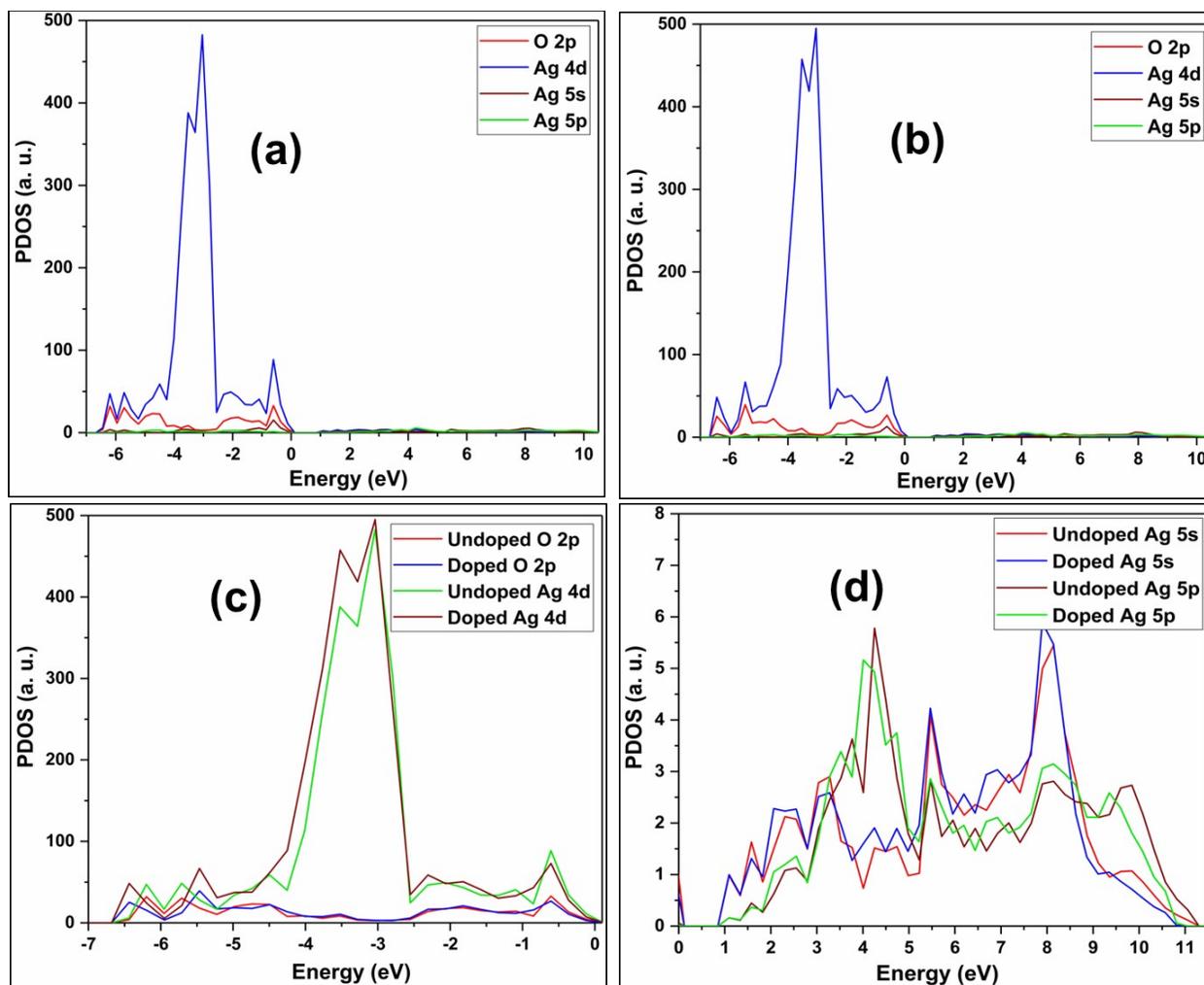
**Fig. S8** Optimized geometries of (a) C0, (b) C1, and (c) C2 models.



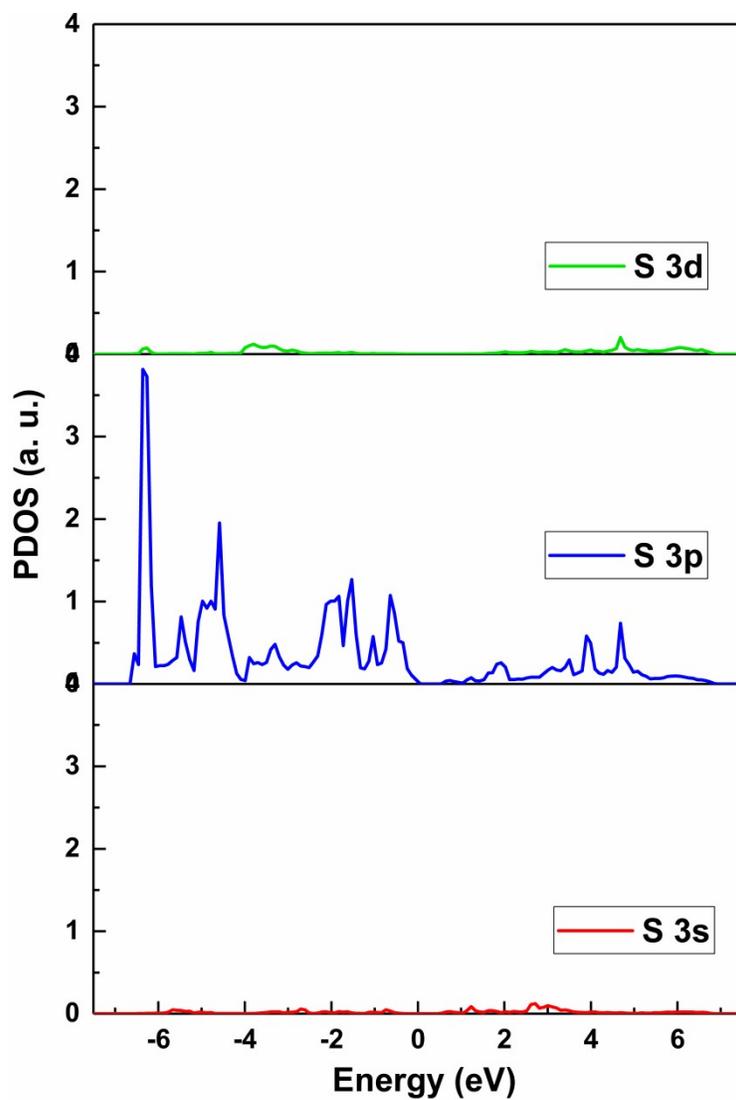
**Fig. S9** Comparison of TDOS of OV Ag<sub>2</sub>O (C1 model) and S doped Ag<sub>2</sub>O system (C2 model).

**Table S4** Change of the lattice parameters on the increment of OV in Ag<sub>2</sub>O lattice

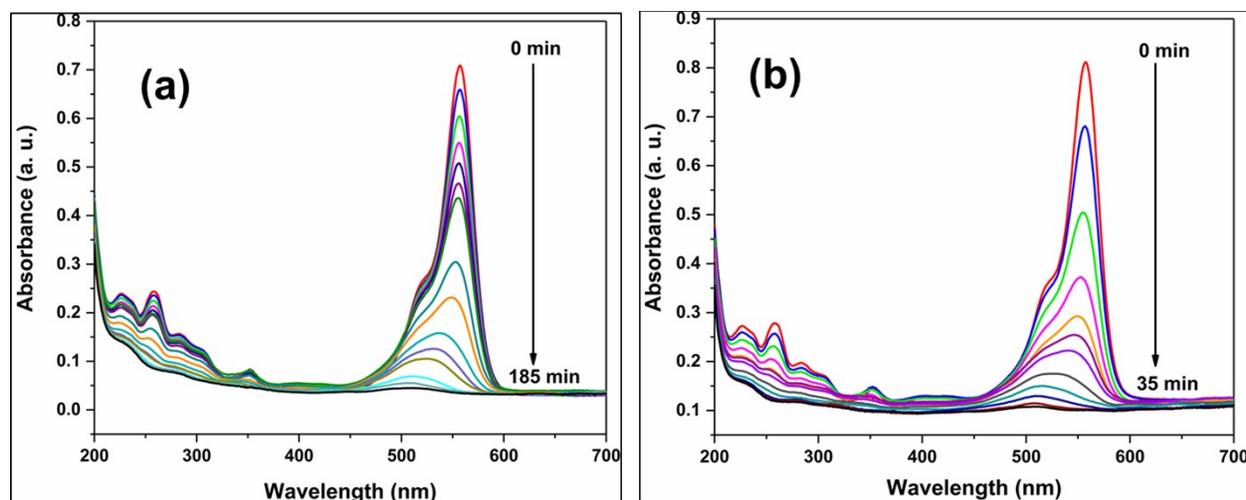
Lattice parameters	Without OV	10V (C1)	20V (C4)
<b>a</b>	9.63	9.53	9.46
<b>b</b>	9.63	9.53	9.45
<b>c</b>	9.63	9.53	9.46
<b>α</b>	90	90	90
<b>β</b>	90	90	90
<b>γ</b>	90	90	90
<b>Volume</b>	894.11	866.38	844.94



**Fig. S10** PDOS of (a) C1 and (b) C2 models; PDOS comparison of (c) VB region of undoped and doped systems and (d) CB region of undoped and doped systems. The PDOS of the valence band contributing orbitals (Ag 4d and O 2p) and the conduction band contributing orbitals (Ag 5s and Ag 5p) of C1 model (undoped) expanded and contracted, respectively, due to its hybridization with the S dopant's orbitals.



**Fig. S11** Comparison of PDOS of the dopant's atomic orbitals.



**Fig. S12** UV-Vis absorbance plot on photodegradation of RhB for the catalyst (a) B0 and (b) B2

### Turnover frequency (TOF) analysis

TOF values of the catalysts were calculated to determine the catalytic efficiency. The TOF determination experiment was similar to the photocatalytic experiments. In a 4 ml quartz cuvette, 3 ml aqueous solution of RhB at pH 3 was transferred and 0.1 mg catalyst was dispersed in it. Then the overall mixture was allowed to keep under stirring dark for 35 minutes before the light irradiation. The wavelength range of the visible light source was 410-720 nm. The SOLAR POWER METER (TM-206 model) was used to measure the power of the incident light. The power was 720 W/m<sup>2</sup> throughout the photocatalytic reaction. The calculation value of TOF as per the given relation below,

$$TOF = \frac{\left[ \frac{\text{Number of moles of reactant}}{\text{Number of grams of catalyst}} \right] \times \text{Yield}}{\text{time}}$$

**Table S5** Turn over frequency (TOF) and rate constant of B0, B1, and B2 catalysts for the photo-degradation of RhB

Catalysts	TOF (mole g <sup>-1</sup> min <sup>-1</sup> )	Rate constant (k <sub>app</sub> ) (min <sup>-1</sup> )
<b>B0</b>	4.79 x 10 <sup>-6</sup>	0.0428
<b>B1</b>	9.75 x 10 <sup>-6</sup>	0.1053
<b>B2</b>	1.18 x 10 <sup>-5</sup>	0.1294

### Recyclability experiment details

The catalyst recyclability experiments were performed on a larger scale. 600 μL 40 ppm RhB dye solution was added to 6 ml deionized double distilled water (DDDW) with the addition of 21 μL 1(M) HCl. The final pH of the aqueous solution of the dye was ~3. Next, 17 mg solid photocatalyst was added to the prepared dye solution. The whole solution was sonicated until the proper dispersion of the photocatalyst. Then the whole mixture was kept in the dark with continuous stirring for 10 minutes to ensure adsorption-desorption equilibrium. Only after that, the mixture was allowed for the LED light irradiation. In the 1<sup>st</sup> cycle, the catalyst degraded 50% of RhB in 5 minutes. Then, the used catalyst was washed several times with the DDDW for the next cycles. All the cycles gave the same degradation ability in the 5 minutes of light irradiation. Here, in the 1<sup>st</sup> cycle, we assumed the degradation as 100% and comparatively followed rest cycles.