

*Electronic Supplementary Information for*

**Elucidating Electronic Structures of  $\beta$ -Ag<sub>2</sub>MoO<sub>4</sub> and Ag<sub>2</sub>O Nanocrystals via Theoretical and Experimental Approaches towards Electrochemical Water Splitting and CO<sub>2</sub> Reduction**

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## **Synthesis of Ag<sub>2</sub>O**

Ag<sub>2</sub>O powder were prepared by the hydrothermal method at 160 °C for 2 h through mixing silver nitrate (30ml,0.1M) and sodium hydroxide (60ml, 2M), then transferring into a stainless-steel autoclave. The hydrothermal processing creates favorable conditions for chemical reactions between the Ag<sup>+</sup> and O<sup>2-</sup> ions, which results in the formation of crystalline Ag<sub>2</sub>O. After cooling the stainless-steel autoclave to room temperature, the resulting suspensions were washed several times with deionized water to remove residual ions. Finally, Ag<sub>2</sub>O precipitated were collected and dried at 80 °C for 2 h.

## **Characterization of Ag<sub>2</sub>O crystals**

Crystal structure of Ag<sub>2</sub>O was determined using X-ray diffraction (XRD) pattern with PANalytical diffractometer, The Netherlands, with k<sub>α</sub>-Cu ( $\lambda=1.54060 \text{ \AA}$ ) radiation in the 2 $\theta$  range from 5° to 80° in the normal routine with a scanning velocity of 2°/min. Diffuse reflectance spectroscopy (DRS) was conducted using AvaSpec2048-TEC spectrometer with AvaLight DH-S as light source and for spectral analysis, an illumination range of 220-2200 nm was utilized.

## **X-ray Diffraction (XRD)**

According to the XRD pattern presented in Figure S2, all XRD peaks can be indexed perfectly to a simple cubic crystallize structure of Ag<sub>2</sub>O with space group Pn-3m. Moreover, XRD patterns are in agreement with the respective Joint Committee on Powder Diffraction Standards (JCPDS)

card No 41-1104. The profile of the all XRD peaks are narrow with no characteristic peaks of impurities and other phases.

### **Computational Method for Ag<sub>2</sub>O**

Ag<sub>2</sub>O calculations were performed using Quantum ESPRESSO package. A kinetic energy cutoff of 80 Ry was applied for the plane-wave expansion of the electronic states to obtain a good convergence for total energy and forces acting on the atoms. The convergence threshold of the optimized calculations was a total energy of  $10^{-8}$  Ry. The special points sampling over the Brillouin zone was done with a  $14 \times 14 \times 14$  k-point mesh. For density of states (DOS), the linear tetrahedron method was used.

### **Band structures, density of states (DOS) and electronic density map of Ag<sub>2</sub>O**

In the structure of Ag<sub>2</sub>O, the Ag atoms are linearly coordinated to oxygen atoms, whereas oxygen atoms are in the tetrahedral environment made by Ag atoms. According the density of states plots in the figure S4a, the valence band specified by the hybridization of O 2p and Ag 4d with predominant features of Ag 4d. In addition, s and p states of Ag show non-vanishing contributions within the valence band due to an intra-atomic hybridization of 4d states with s and p states of Ag. The width of the valence band is equal to -6.5eV and Ag 4d states have an intensity peak at -3.4 eV. In the lower part of valence band, the two intensive peaks of O 2p are detected at -6.0 and -4.5 eV respectively. The conduction band consists of Ag 5p states. The total DOS shows that O atomic orbitals have a minimal contribution (between -6 eV and 8eV) due to a weak hybridization between the Ag and O orbitals. On the other hand, the total DOS indicates significant role of Ag 4d orbitals in the VB and CB.

The calculation of band gap using density functional theory and GGA functional usually gives rise to an underestimated value, predicting a metallic system through the overlap of the VB and CB at the  $r$  point that presented in the figure S4b.

In order to realize the nature of the Ag—O bonding, we have calculated the charge density map for the Ag<sub>2</sub>O in the plane 01-1. According the Figure S5, the spherical distribution of electron density in the center of the oxygen nucleus is similar to the distribution of the electron density in Ag.

The electron density decreases in the region close to the Ag atom in the Ag-O bond direction and around the Ag that can be an evidence of s-d and p-d intra-atomic hybridizations. We find that the bonding character of the Ag-O bond is more ionic.

Supporting Information Figures:

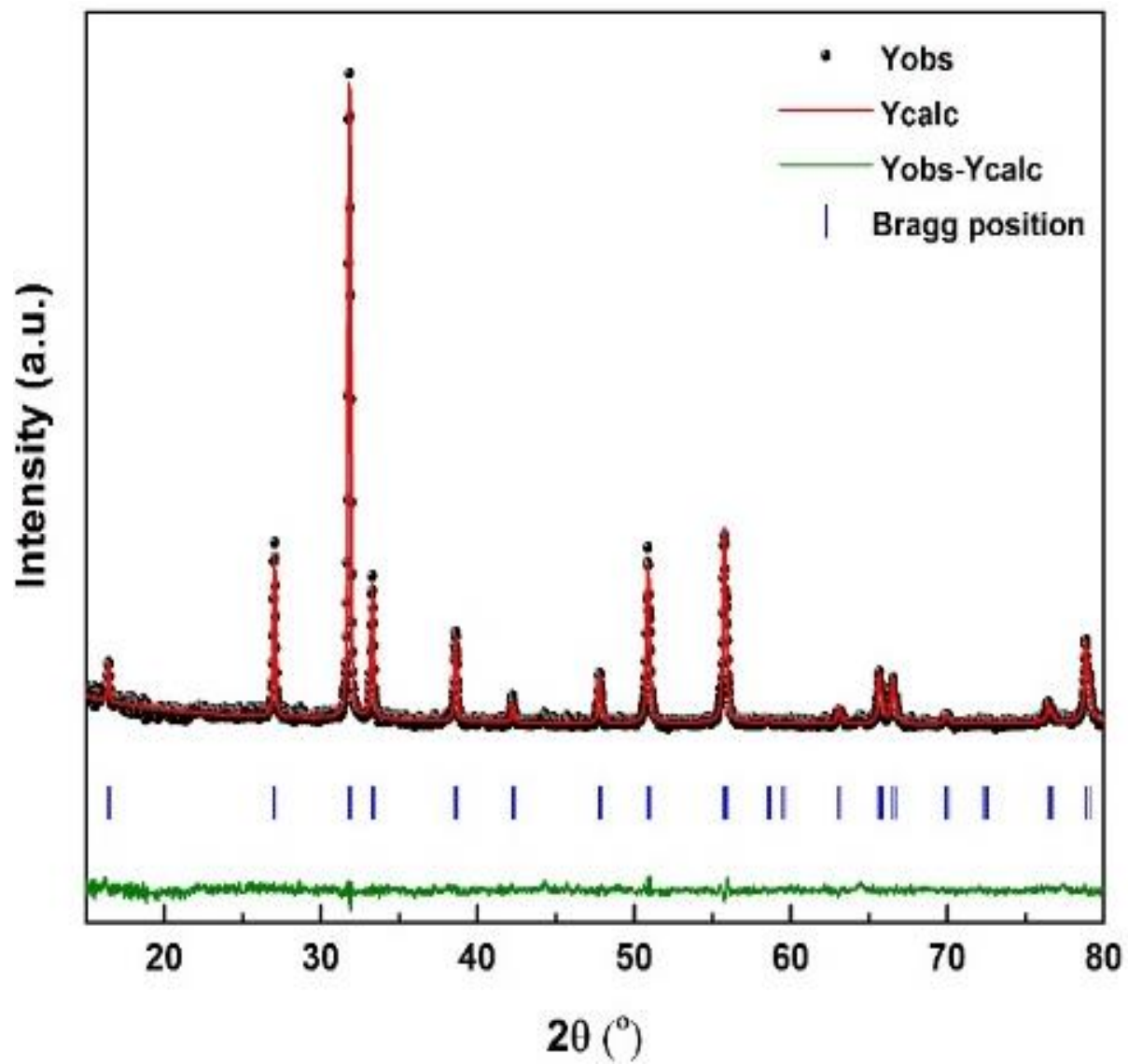
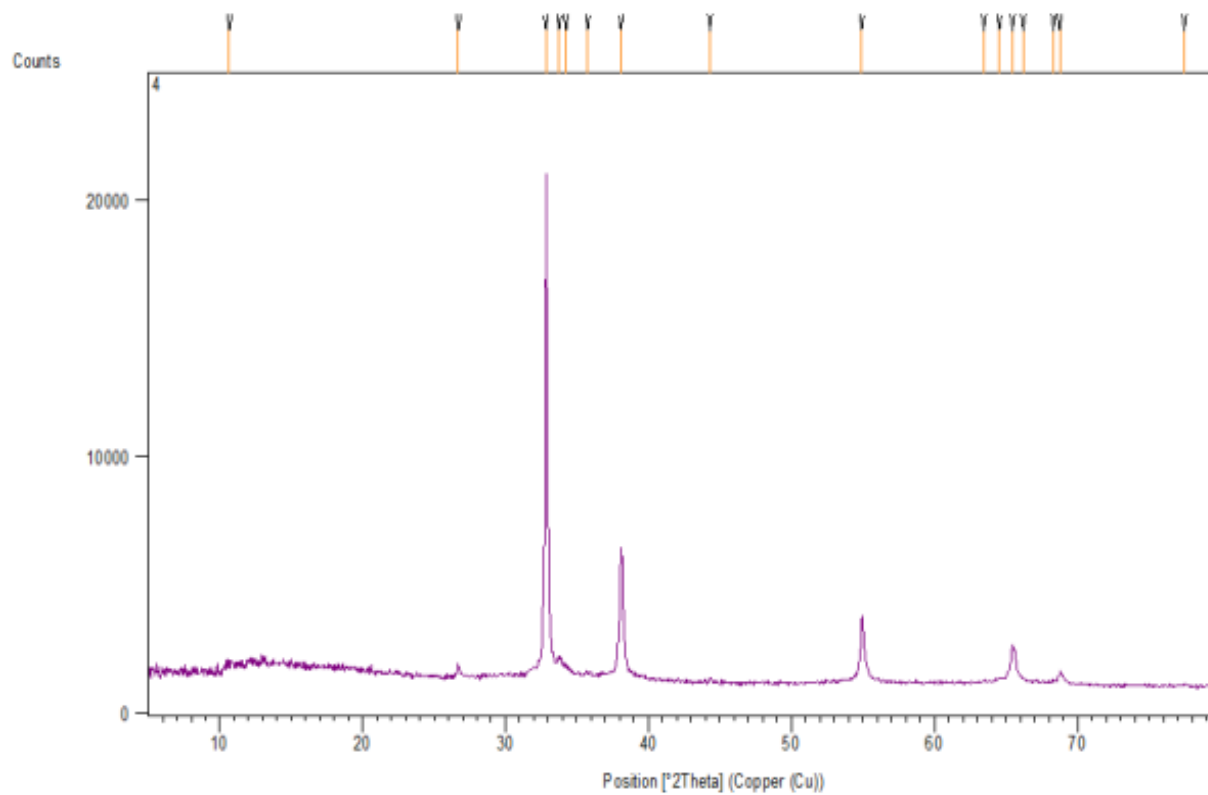
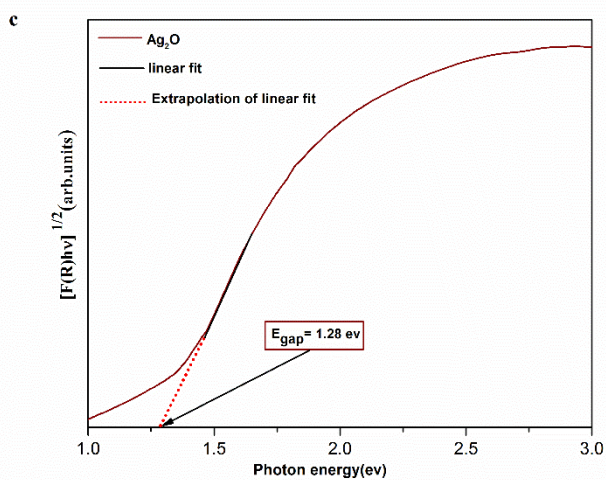
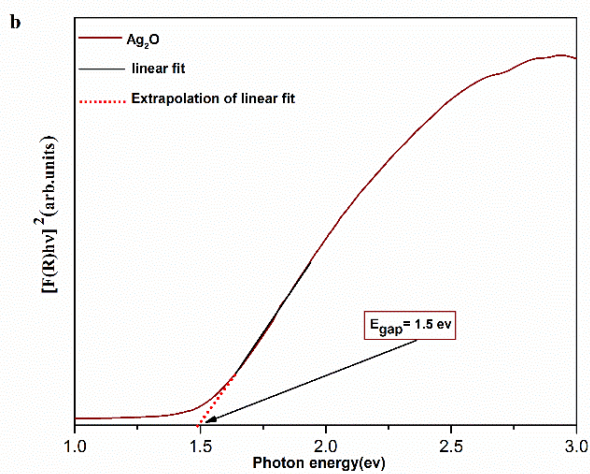
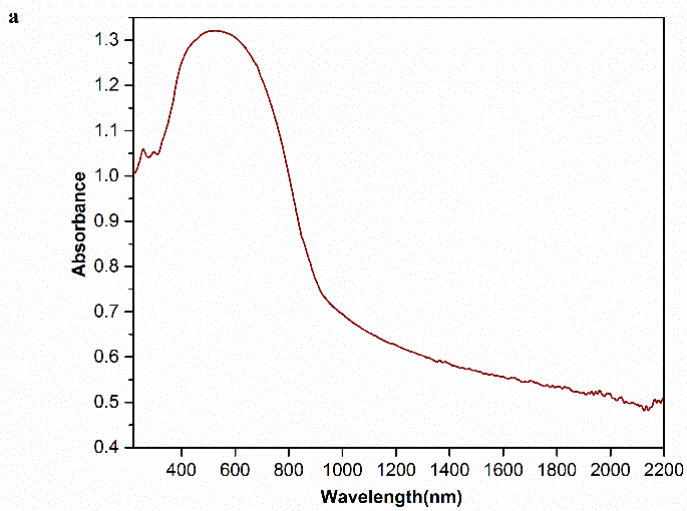


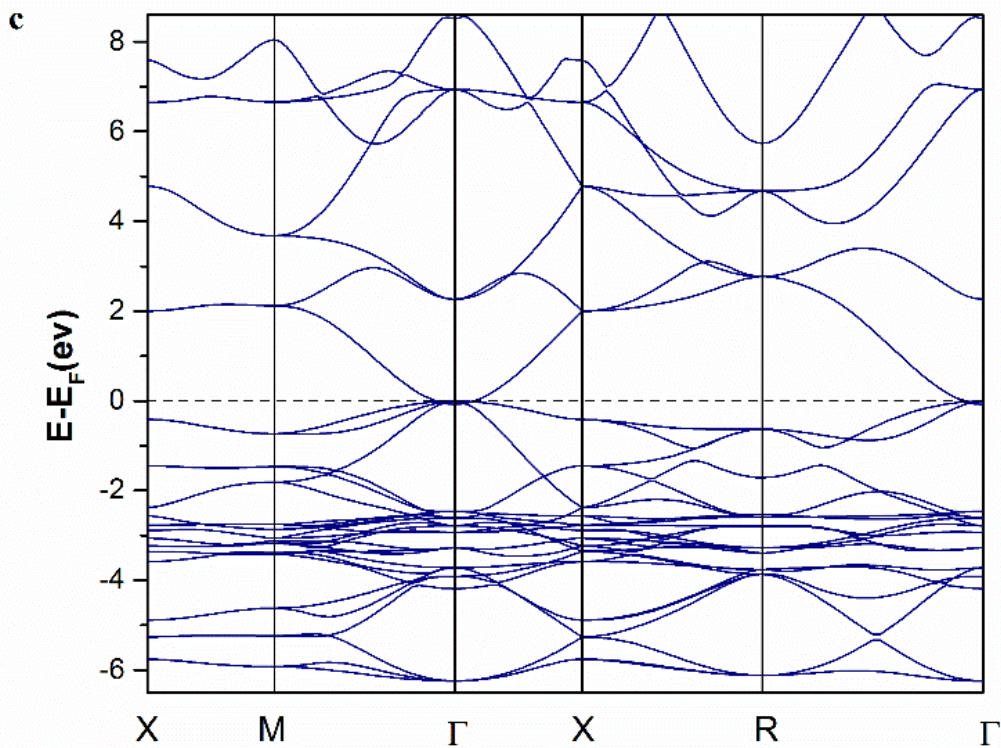
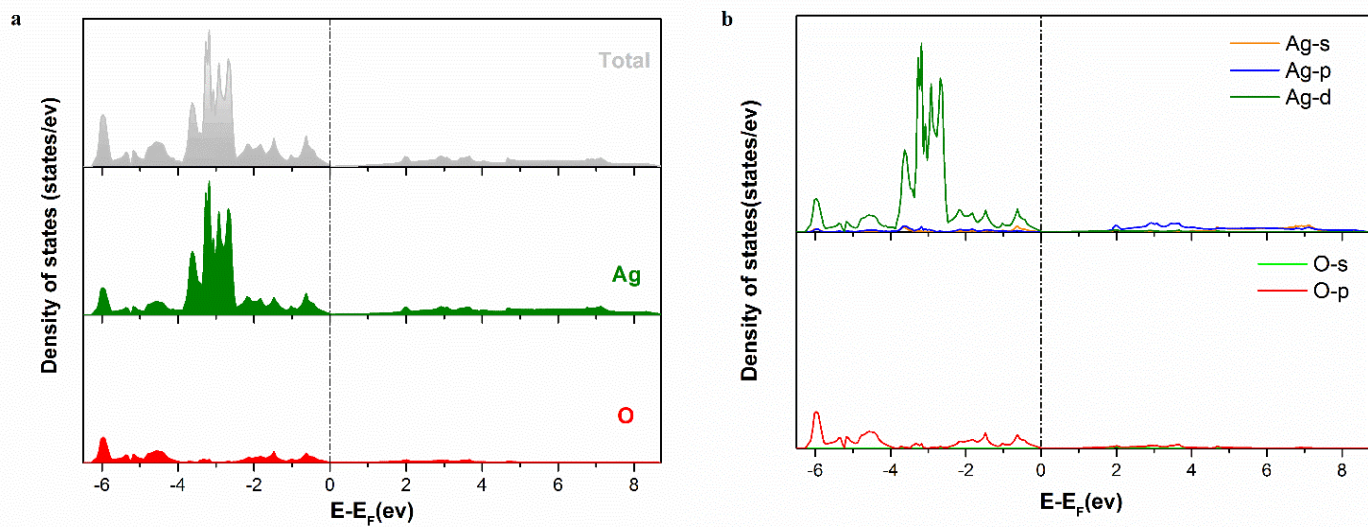
Figure S1. Rietveld refinement plot for  $\beta\text{-Ag}_2\text{MoO}_4$



**Figure S2.** XRD pattern for Ag<sub>2</sub>O.

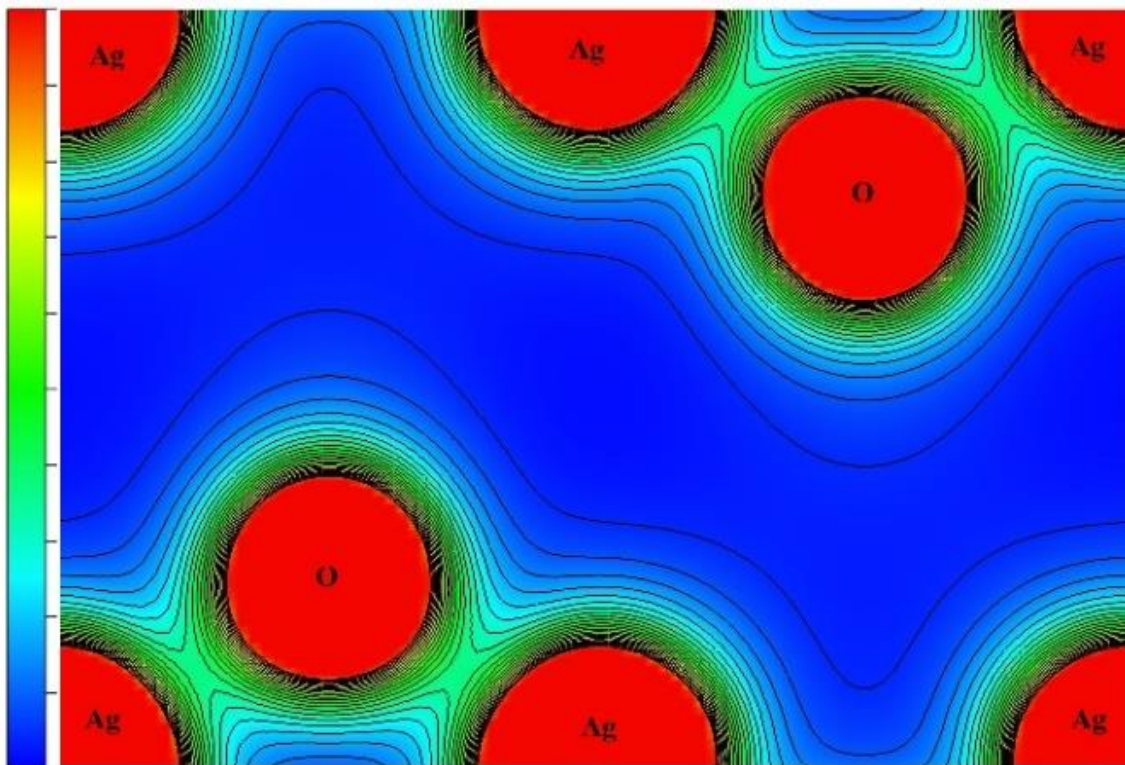


**Figure S3.** a) Diffuse reflectance UV-Vis spectra; b) direct electronic transitions; c) indirect electronic transitions of  $\text{Ag}_2\text{O}$ .

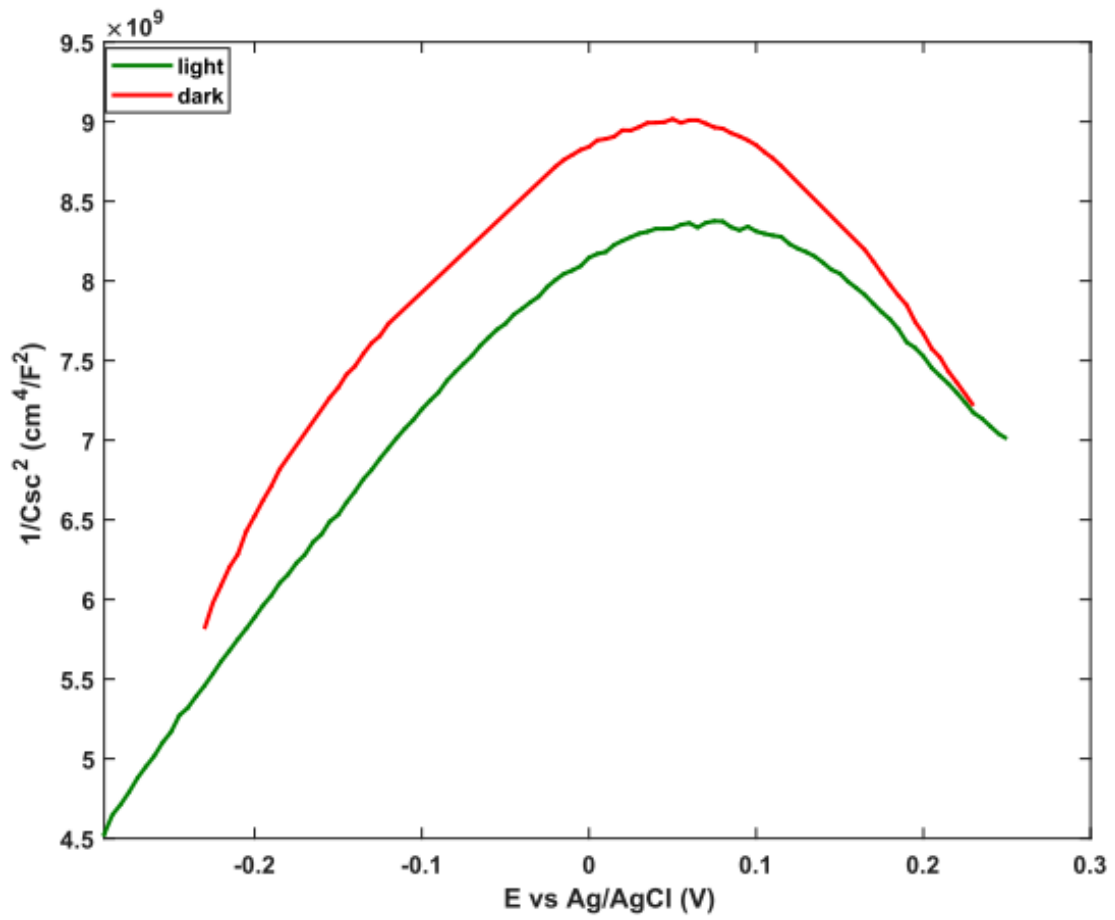


**Figure S4.** a) DOS and b) PDOS c) band structures of  $\text{Ag}_2\text{O}$ .





**Figure S5.** Contour maps of electron densities for (01-1) crystallographic plane of Ag<sub>2</sub>O.



**Figure S6.** Mott-Schottky plots for Ag<sub>2</sub>O in dark and illumination conditions.

**Table S1** Standard errors for both slopes and intercepts achieved at 95% confidence interval.

<b>Sample</b>	<b>Reaction</b>	<b>Linear fit equation</b>	<b>Slope's standard Error</b>	<b>Intercept's standard Error</b>
Ag <sub>2</sub> MoO <sub>4</sub>	OER	$y = 0.312x + 1.4548$	0.0034	0.0146
Ag <sub>2</sub> O	OER	$y = 0.310x + 1.4203$	0.0021	0.0087
Ag <sub>2</sub> MoO <sub>4</sub>	HER	$y = 0.173x + 0.9024$	0.0013	0.0042
Ag <sub>2</sub> O	HER	$y = 0.205x + 0.957$	0.0010	0.0031
Ag <sub>2</sub> MoO <sub>4</sub>	HER (CO <sub>2</sub> )*	$y = 0.367x + 1.685$	0.0018	0.0058
Ag <sub>2</sub> O	HER (CO <sub>2</sub> )*	$y = 0.356x + 1.705$	0.0001	0.0020

\*Hydrogen evolution in the presence of CO<sub>2</sub>