Supporting Information

Ag-Boosted $CoO_x/BiVO_4$ p-n Heterojunction for Efficient Photoelectrochemical Water Splitting

Zhouchen Li [a,1], Linyao Deng [a,1], Tingting Liu[a], Yihui Chen[a], Yutong Guo [a], Jingwei Huang [a *]

[a] College of Chemistry and Chemical Engineering, Gansu International Scientific and Technological Cooperation Base of Water-Retention Chemical Functional Materials, Northwest Normal University, Lanzhou 730070, China

[*] Corresponding author. E-mail: huangjingwei2009@163.com, huangjingwei@nwnu.edu.cn

[1] These authors contributed equally to this work

Supplementary Figures

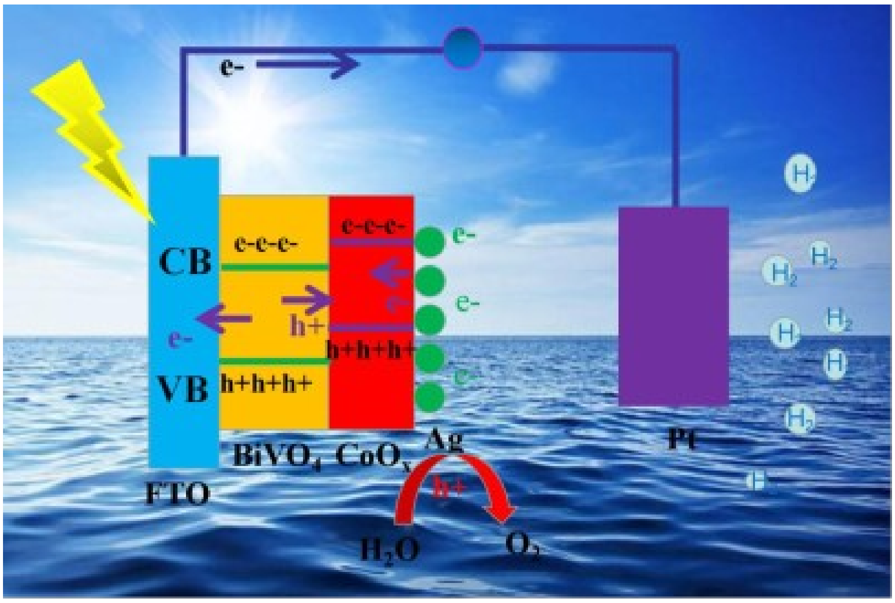

Fig. S1. Schematic illustration for the charge transfer and separation as well as PEC water splitting process of $BiVO_4/CoO_x/Ag$ architecture under visible light illumination.

As shown in Fig. S1, under simulated solar illumination from the backside, the $BiVO_4/CoO_x/Ag$ photoanode undergoes charge generation via photon absorption. Within the n-type $BiVO_4$ semiconductor, electrons are excited to the conduction band (CB) while holes remain in the valence band (VB). Concurrently, the p-type CoO_x layer generates electron-hole pairs upon illumination. A type-II p-n heterojunction forms due to band alignment mismatch between $BiVO_4$ and CoO_x, establishing a built-in electric field at their interface. This field drives electrons from the CoO_x CB to the $BiVO_4$ CB, followed by migration through the external circuit to the Pt counter electrode for water reduction. Simultaneously, holes transfer from the $BiVO_4$ VB to the CoO_x VB, facilitating water oxidation at the electrode-electrolyte interface. Plasmonic excitation of Ag nanoparticles under illumination generates hot electrons that inject into the CoO_x CB. This process synergistically accelerates electron transport and suppresses charge recombination.

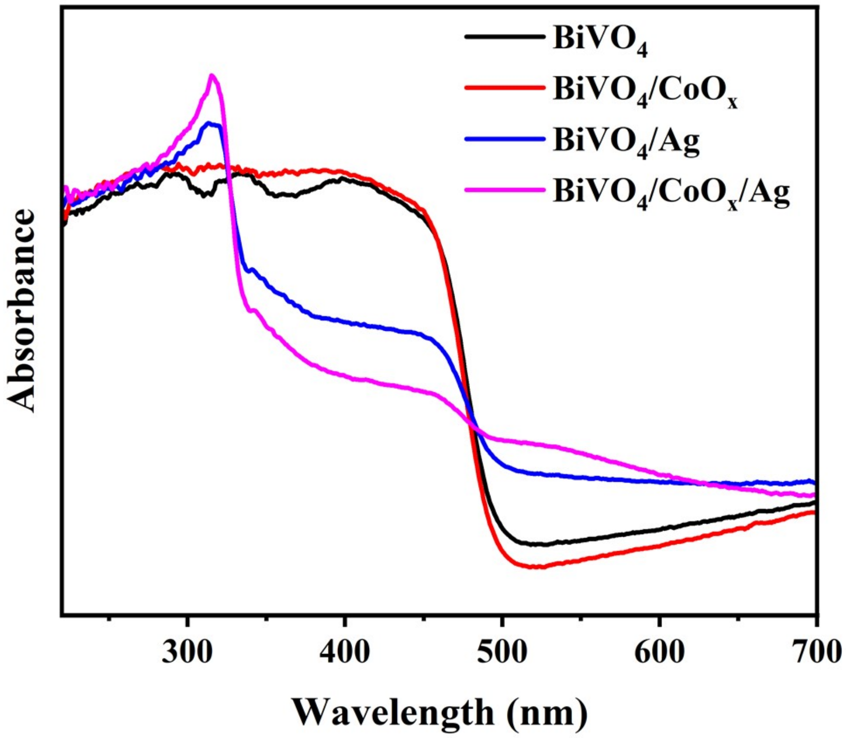

Fig. S2. UV-vis DRS of $BiVO_4$, $BiVO_4/CoO_x$, $BiVO_4/Ag$ and $BiVO_4/CoO_x/Ag$.

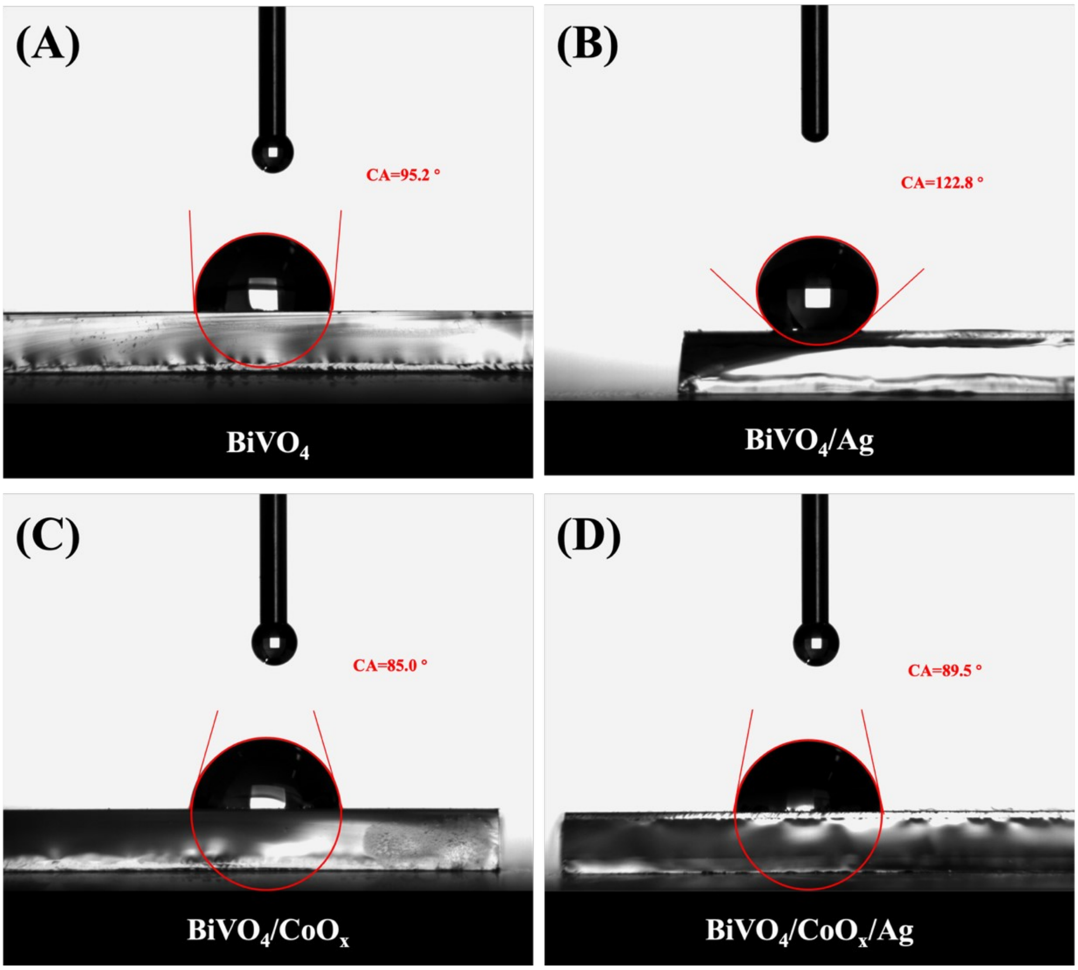

Fig. S3. Static water contact angle tests of (A) $BiVO_4$, (B) $BiVO_4/Ag$, (C) $BiVO_4/CoO_x$, (D) $BiVO_4/CoO_x/Ag$.

As shown in Fig. S3, static water contact angle (CA) measurements reveal distinct interfacial properties: $BiVO_4/Ag$ exhibits strong hydrophobicity (CA = 122.8°), attributed to the low surface energy of metallic Ag. In contrast, hydroxyl-rich CoO_x enhances hydrophilicity when deposited on $BiVO_4$ (CA = 85.0°). The ternary $BiVO_4/CoO_x/Ag$ system demonstrates moderated hydrophilicity (CA = 89.5°) compared to pristine $BiVO_4$ (CA = 95.2°), suggesting synergistic interfacial modification. This optimized surface wettability facilitates electrolyte diffusion across the electrode-electrolyte interface, thereby enhancing photocurrent density during water oxidation.

Table S1 Quantitative values obtained from the equivalent circuit for all electrodes.

Electrodes	$R_s(\Omega)$	$R_{ct}(\Omega)$
$BiVO_4$	20.3	966.0
$BiVO_4$(dark)	21.6	1261.0
$BiVO_4$/Ag	23.2	746.0
$BiVO_4$/Ag(dark)	25.7	1069.0
$BiVO_4/CoO_x$	20.7	705.5
$BiVO_4/CoO_x$(dark)	22.5	1292.0
$BiVO_4/CoO_x$/Ag	22.3	190.4
$BiVO_4/CoO_x$/Ag(dark)	23.5	1306.0