Supporting Information for

Synergistic Effect of Ag@CN with BiVO₄ in a Unique Z-Type Heterojunction for Enhancing Photoelectrochemical Water Splitting Performance

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1. Experimental Section

1.1. Materials

Melamine (MA), Cyanuric acid (CA), Citric acid (CTA), $AgNO_3$, HNO_3, PVP, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_{10}H_2(W_2O_7)_6\cdot xH_2O$, $Bi(NO_3)_3\cdot 5H_2O$, NH_4VO_3, PEG-600, ethylene glycol and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), FTO glass was purchased from Baisite Co., Ltd. All solutions involved in the experiments were prepared with deionized water (18.25 MΩ, Molewater System Co., Ltd.).

1.2. Fabrication of carbon nitride (CN) and Silver-loaded carbon nitride (Ag@CN)

Firstly, dissolve 1.26 g of melamine and 1.23 g of cyanuric acid in 50 mL of ultrapure water to form solutions A and B, respectively. Then, dissolve 0.096 g of citric acid and 0.042 g of silver nitrate in 20 mL of ultrapure water to prepare solution C. Gradually add solution C to solution B, stirring continuously for 10 min. Combine this mixture with solution A and stirred at room temperature for 6 h. Collect the product by centrifugation, wash it three times with deionized water and ethanol, and dry overnight in a vacuum oven. Finally, heat the dried product under an argon atmosphere to 600°C at a rate of 5°C/min for 4 h.

For the preparation of CN, follow the same steps as for Ag@CN, but without adding the silver nitrate solution.

1.3. Preparation of Ag nanoparticles

Ag nanoparticles were also prepared using a solvothermal method. First, 0.2 g AgNO$_3$ was dissolved in 20 mL of 1 M aqueous nitric acid and completely dissolved by sonication. Subsequently, 80 mL of ethylene glycol containing 0.28 g PVP was added to the above mixture. After thorough stirring, the mixture was transferred to the liner of a 100 mL reactor and kept at 160℃ for 10 h. After cooling to room temperature, the Ag nanoparticles were separated by centrifugation and washed three times with ethylene glycol, and the grey precipitate was dried in an oven at 60℃ for 12 h.

1.4. Fabrication of Mo,W:BVO, Mo,W:BVO/Ag, Mo,W:BVO/CN, Mo,W:BVO/Ag@CN, Mo,W:BVO/Ag@CN-S photoanodes

The creation of Mo,W:BVO prelim solvents requires merging three solutions: (1) 3.75 mM of Bi(NO$_3$)$_3$ liquified in 500 μL of ethylene glycol. (2) 500 μL of 3.75 mM NH$_4$VO$_3$ ethylene glycol solution, which holds 3% of (NH$_4$)$_6$Mo$_7$O$_{24}$ and (NH$_4$)$_{10}$H$_2$(W$_2$O$_7$)$_6$, respectively. (3) PEG-600 weighing 0.009 g is liquified in 250 μL of ethylene glycol. Utilizing 200 μL of the initial solution, it is progressively applied onto the FTO glass substrate, then air-dried in a 130°C setting for 60 min to vaporize the solvent. Subsequently, a muffle furnace subjects it to a 500°C setting for 150 min producing Mo,W:BVO photoanodes.

The prepared 3 mg g Ag@CN was dissolved in 1 mL of ethylene glycol, then different amounts were added to the BVO precursor solution, mixed well and 200 μL was applied dropwise to the FTO, dried at 130°C for 1 h and then annealed in

a muffle furnace at 500°C for 3 h. The mass fraction of Ag in the best performing photoanode was measured to be 0.33%.

The preparation of Mo,W:BVO/Ag and Mo,W:BVO/CN photoanodes was similar to that of Mo,W:BVO/Ag@CN by replacing Ag@CN with a glycol solution of Ag nanoparticles and CN respectively and adding it to the BVO precursor.

Mo,W:BVO/Ag@CN-S photoanodes were obtained by a simple spin-coating method. The Ag@CN solution was coated onto the prepared Mo,W:BVO films and spun at 1200 r/min for 60 s to ensure uniform distribution and to shake off the excess solution. Finally, they were dried in an oven at 130°C for 1 h.

1.5. Fabrication of Mo,W,Ag:BVO photoanodes

The preparation of the Mo,W,Ag:BVO photoanode is similar to that of Mo,W:BVO, except that 5% of Ag is added through $AgNO_3$ while adding 3% of Mo and W.

1.6. Characterization

Scanning electron microscopy (SEM) measurements were conducted on using a field-emission scanning electron microscope (JSM-7800F, JEOL, Tokyo, Japan) operated at an accelerating voltage of 5 kW. X-ray photoelectron spectroscopy (XPS) measurements were examined on a PHI 5000 Versa Probe III (Chanhassen, MN, USA). X-ray diffraction (XRD) patterns were performed on a Rigaku Ultima IV instrument (Tokyo, Japan) utilizing Cu Kα radiation (40 kW). Transmission electron microscopy (TEM) images were performed on a JEOL JEM-2100 Plus

transmission electron microscope (Tokyo, Japan). Ultraviolet visible (UV-vis) absorption spectra was carried out on a Ultraviolet-Visible Spectrophotometer (UV-2700, Tokyo, Japan). Ultraviolet absorption spectrum was carried out on the UV-2700 ultraviolet spectrophotometer (Shimadzu, Japan).

1.7. Photoelectrochemical examination

BVO-based films were used as the photoanode in a 3-arm PEC cell. The PEC performance under AM 1.5 G irradiation was recorded with a CHI-660D potentiostat in a sandwich-type configuration using Pt slice as the counter electrode, saturated calomel electrode (SCE) as the reference, and Na_2SO_4 solution (0.1 M) as electrolyte. A 300 W xenon arc lamp equipped with a simulated solar light filter (HSX-F300, Beijing NBeT Technology Co., Ltd) calibrated to 100 mW/cm², which was measured with a radiometer (CEL-NP2000, Beijing Au-light Co., Ltd), was used as the light source. EIS Nyquist plots were obtained at 0.6 V with AC amplitude of 5 mV in the frequency range of 0.1-105 Hz. The charge separation efficiency (η_{trans}) was obtained using the following formula:

$$\eta_{trans} = \frac{J_{H_2O}}{J_{hole}} \times 100\%$$

where J_{H_2O} and J_{hole} denote the photocurrent density obtained by measuring the LSV curve in the absence and presence of the trapping agent, respectively. The incident photo-to-current conversion efficiency (IPCE) was calculated according to the following formula:

$$IPCE = \frac{1240 \times I}{\lambda \cdot P} \times 100\ \%$$

in which I indicate the photocurrent density measured at each wavelength of light,

and λ and P indicate the wavelength and intensity of the monochromatic light.

The ABPE can be calculated by the photocurrent-potential curves (LSV) using

the equation:

$$ABPE = \left[J_{H2O} \times \frac{1.23 - V}{P} \right] \times 100\%$$

where J_{H2O} is the photocurrent density (mA/cm^2), V is the applied bias (V_{RHE}) and

P is the incident illumination power density (100 mW/cm^2). The band-gap

energies were according to the equation:

$$\lambda_g = 1240/E_g$$

where λ_g is the band-gap wavelength and E_g is the band-gap energy.

2. Supplementary Figures
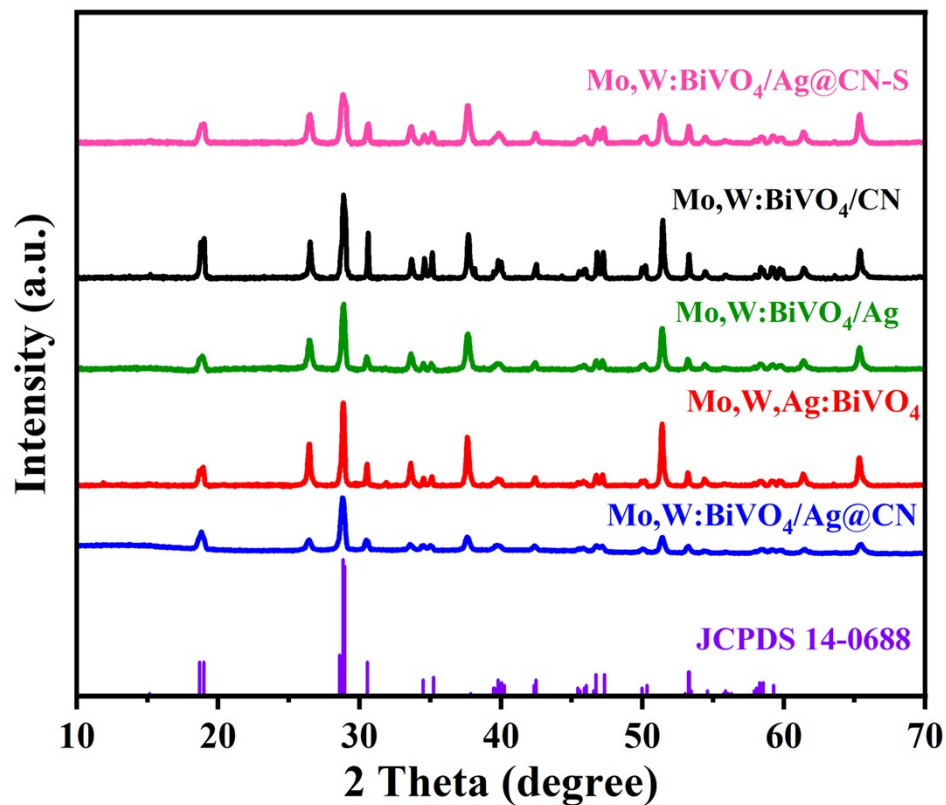
Fig. S1 XRD patterns of Mo,W:BVO/Ag@CN, Mo,W:BVO/Ag, Mo,W:BVO/CN, Mo,W:BVO/Ag@CN-S.
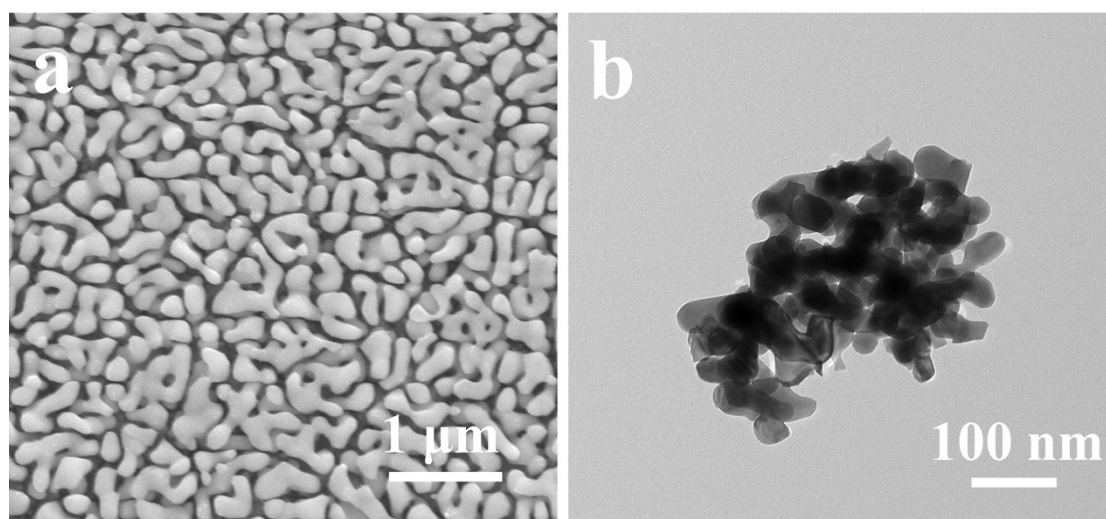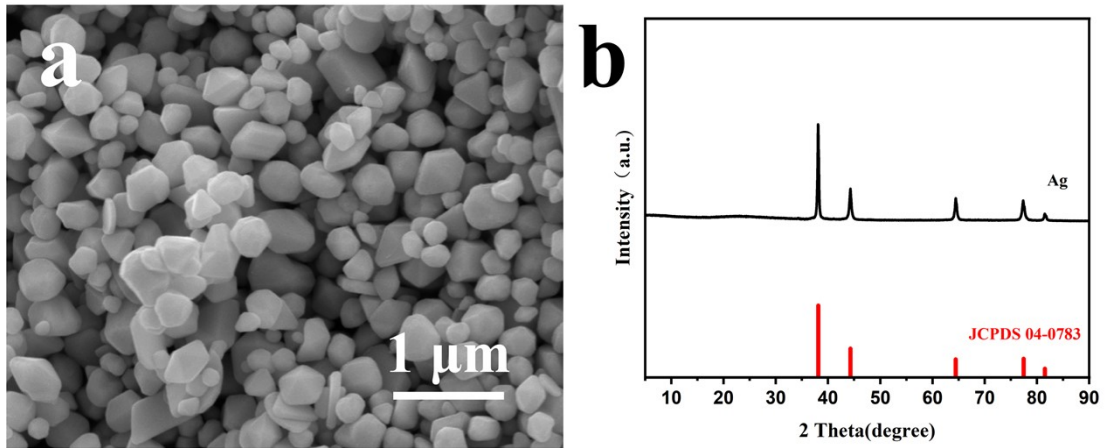

Fig. S2 SEM (a) and TEM (b) image of Mo,W:BVO.

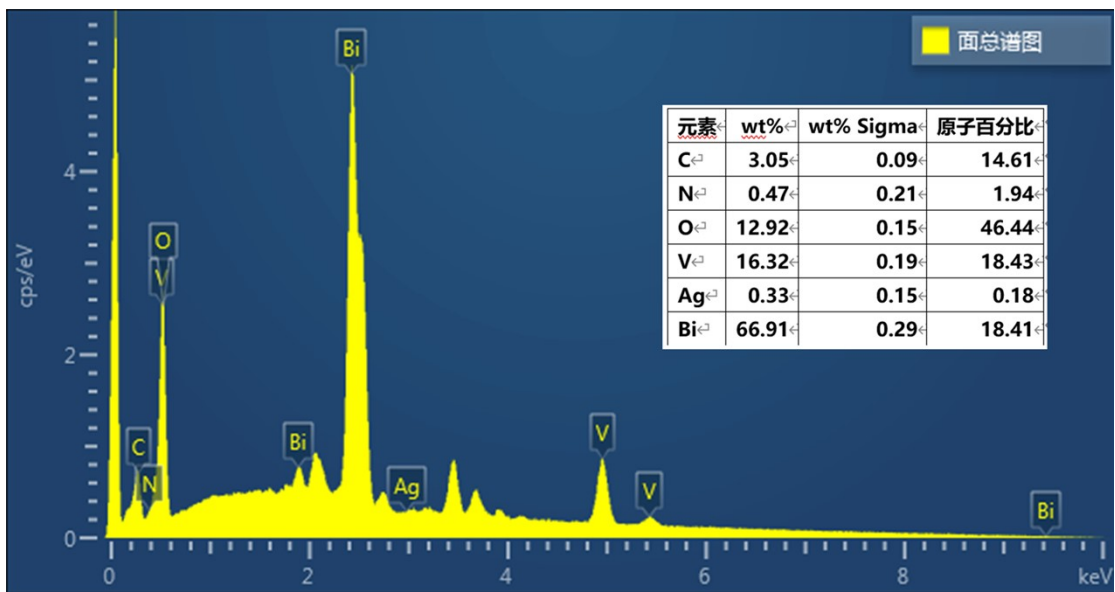**Fig. S3** SEM (a) and XRD (b) images of Ag nanoparticles.

元素	wt%	wt% Sigma	原子百分比
C	3.05	0.09	14.61
N	0.47	0.21	1.94
O	12.92	0.15	46.44
V	16.32	0.19	18.43
Ag	0.33	0.15	0.18
Bi	66.91	0.29	18.41

Fig. S4 EDS elemental distribution map of Mo,W:BVO/Ag@CN.

	Wt%	σ
C	67.7	0.5
N	29.0	0.4
Ag	3.4	0.3
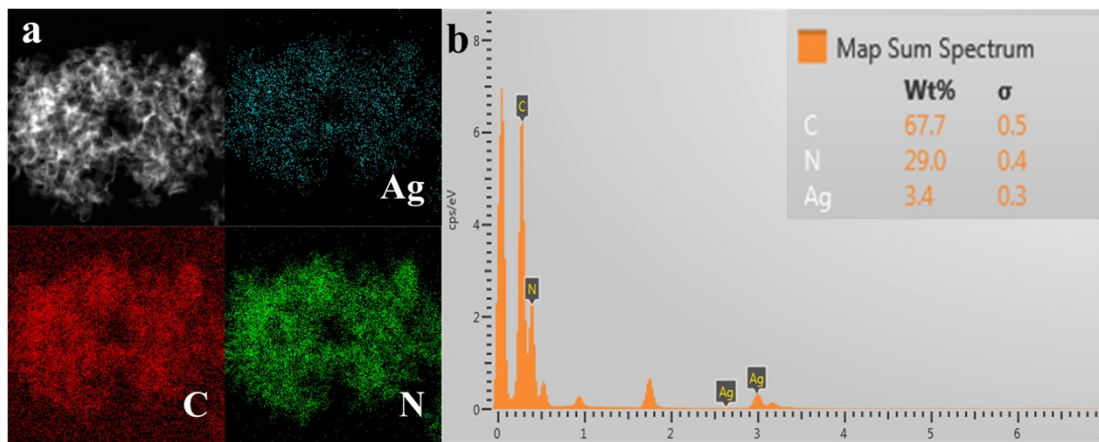
Fig. S5 Ag@CN of EDS elemental mapping (a) and EDS elemental distribution map (b).
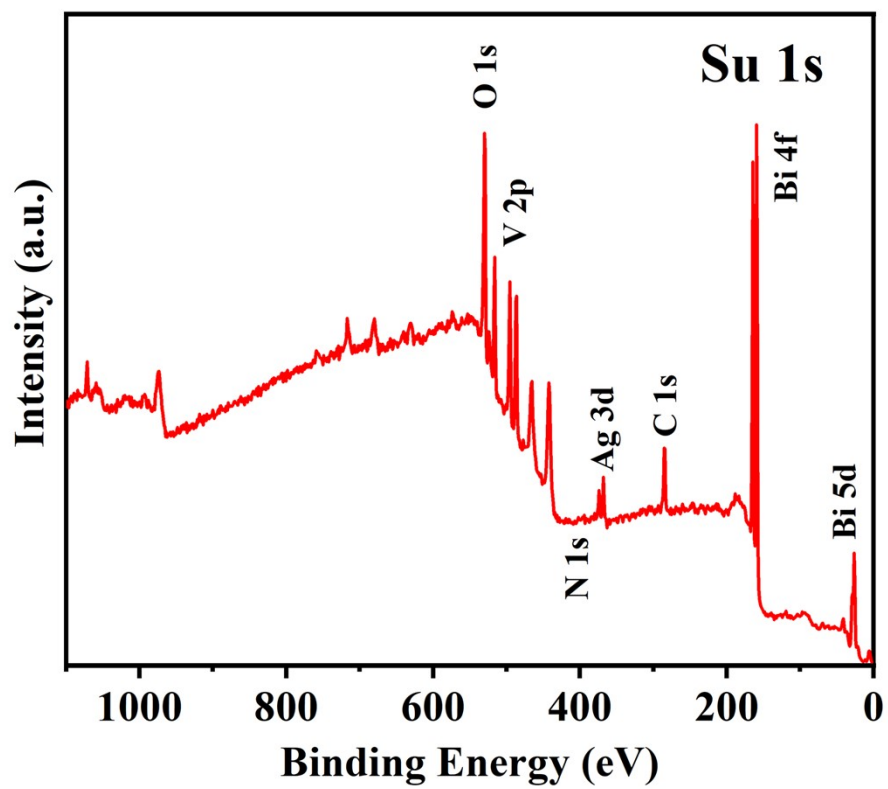
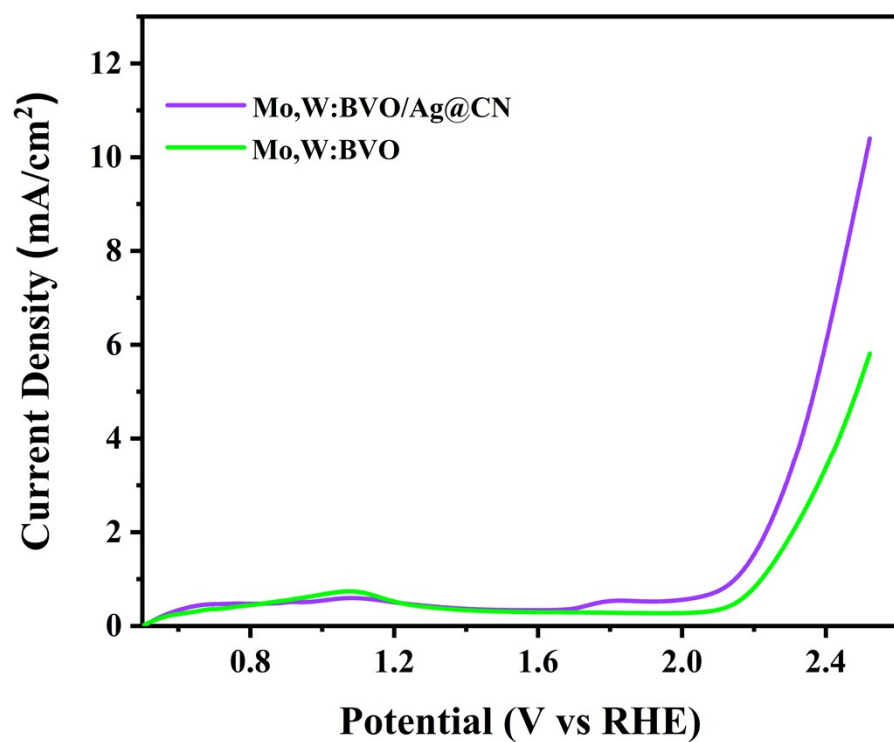**Fig. S6** XPS survey spectra of Mo,W:BVO/Ag@CN.

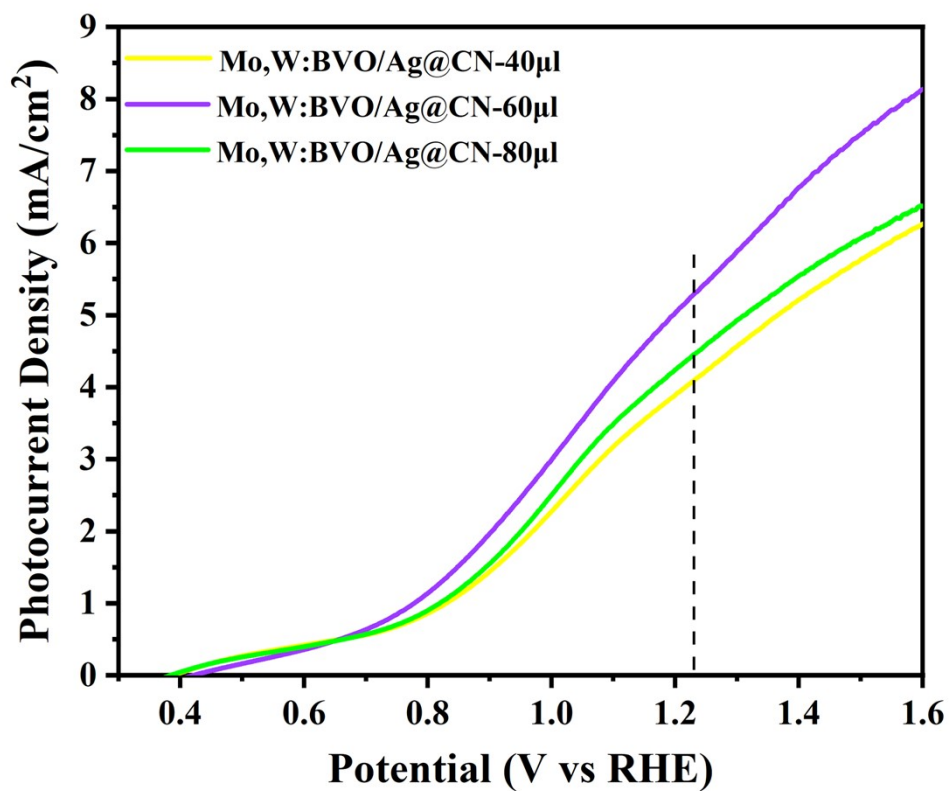**Fig. S7** LSV in the dark of BVO-based photoelectrodes.

Fig. S8 LSV curves for different Ag@CN additions of BVO-based photoelectrodes.