**Supporting Information**

**Influence of Bi-Cu Microstructure on the Photoelectrochemical Performance of BiVO4 Photoanode for Efficient Water Splitting**

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**Chemicals**

Bismuth nitrate pentahydrate (Bi(NO3)3.5H2O), sodium selenite (Na2SeO3), acetic acid (CH3COOH), ethanol (C2H5OH) and sodium sulfate (Na2SO4) were purchased from Aldrich. Nitric acid (HNO3), vanadyl acetylacetonate, copper nitrate (Cu (NO3)2) were purchased from Merck. TiO2 paste (18NR-T) used for electrode preparation was obtained from Dyesol. Deionized water (resistivity ~18.2 Ω cm) was obtained from a Millipore Direct-Q3 UV system. Fluorine doped Tin oxide (FTO) glass used (sheet resistance ~25 Ω cm-2) was purchased from Pilkington.

**Characterization**

The absorption spectra of the synthesized electrodes were recorded on a UV-Vis spectrophotometer (Shimadzu UV-3600). Powder X-ray diffraction (XRD) patterns of samples were measured on a PANalytical, Xpert PRO instrument. Surface morphologies of the samples were analyzed using a field emission scanning electron microscope (FESEM-Zeiss supra 40). The chemical stoichiometry of the Bi-Cu/BiVO4 sample was characterized using X-ray photoelectron spectroscopy (XPS; AXIS Supra-Kratos analytical spectrophotometer) with Mg Kα monochromatic excited radiation of 1253.6 eV. High-resolution transmission electron microscope (HR-TEM) images were recorded using a TECNAI G-2 FEI instrument operating at 300 kV while samples were deposited on copper grids. PEC measurements were performed in an aqueous electrolyte of 0.1 M Na2SO4, using a three-electrode system with fabricated films used as working electrode, Pt and Ag/AgCl as the counter and reference electrodes, respectively. Current versus potential (I-V) characteristics of photoanodes were recorded using a LOT-Oriel-Autolab with a 150 W Xenon arc lamp with 100 mW cm-2 intensity (1.5 Airmass filter). The irradiance intensity was confirmed by calibrating with a 2 cm x 2 cm Si Reference Cell and re-affirmed with a radiant power meter from Newport (842-PE). Chronoamperometric (I-t) studies, Mott-Schottky plots, cyclic voltammetry and electrochemical impedance spectra (EIS) were measured on an Autolab PGSTAT 302N equipped with NOVA 2.1 software. Incident photon current conversion efficiency (IPCE) was measured by the Quantum Efficiency Measurement System (Oriel IQE-200), where a 250 W quartz tungsten halogen lamp was used as a light source. A Trace-1310 GC equipped with a TCD was used to quantify hydrogen gas.

**XRD studies**

BiVO4 has monoclinic crystal lattice with (110), (121), (040), (200), (112), (112), (240), (202), (161) and (321) crystal planes at d-spacing values = 4.71, 3.09, 2.94, 2.61, 2.23, 1.95, 1.82, 1.71 and 1.56 respectively (JCPDS NO-140688). Bi NPs have rhombohedral crystal lattice with (012), (104), (110), (202), (024) and (112) planes corresponding to d-spacing of 3.25, 2.34, 2.25, 1.85, 1.61 and 1.42 Å respectively (JCPDS: 851331). Cu NPs shows planes at (111), (200) and (220) of the face centered cubic lattice (JCPDS-892838) which corresponding to d = 2.07, 1.81 and 1.26 Å.

**XPS studies:**

**Chart, histogram

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**Fig. S1** High-resolution XPS region spectra of (a) Bi 4f for BiVO4, BiVO4/Bi and BiVO4/Bi-Cu composite, and (b) Cu 2p for BiVO4/Cu and BiVO4/Bi-Cu nanocomposite.

**TEM images**



**Fig. S2** (a) FE-SEM image, (b) elemental mapping analysis, (c) EDAX images (d) HRTEM images, (e) lattice fringes and (f) SAED patterns of Bi-Cu ANPs.



**Fig. S3** (a), (b) and (c) HRTEM images of BiVO4 sample.

**Reversible Hydrogen electrode (RHE) conversion:**

The measured applied potential versus Ag/AgCl was converted into reversible hydrogen electrode (RHE) by using Nernst equation.

E RHE = E Ag/AgCl + E°Ag/AgCl + 0.059 pH (1)

In equation (1), E°Ag/AgCl is standard electrode potential of Ag/AgCl (0.197 V) at 25 °C and the pH of electrolyte is 7.

**Solar to hydrogen conversion (STH):**

The solar to hydrogen conversion efficiencies (η) of the photoelectrodes for PEC hydrogen evolution reaction was calculated using the following equation:

η = J (1.23 - V)/ Plight  (2)

where, Plight, J and V are the illumination intensity (100 mW cm-2), photocurrent density at the measured bias and applied potential versus RHE, respectively.



**Fig. S4** Bode plots of pristine BiVO4, BiVO4/Cu NPs, BiVO4/Bi NPs and BiVO4/Bi-Cu electrode.

**Table 1.** Impedance data after fitting plots of the pristine BiVO4, BiVO4/Cu NPs, BiVO4/Bi NPs and BiVO4/Bi-Cu photoanodes.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | RS (Ω) | RCT (Ω) | CPE  (µΩ-1) |
| (1) BiVO4 | 9.01 | 196 | 11.5 |
| (2) BiVO4/Cu NPs | 8.62 | 54.1 | 17.4 |
| (3) BiVO4/Bi NPs | 8.56 | 37.5 | 25.2 |
| (4) BiVO4/Bi-Cu NPs | 8.11 | 21 | 28.1 |

**M-S plots:**

**Chart, scatter chart

Description automatically generated**

**Fig. S5** M-S plots of the pristine BiVO4, BiVO4/Cu NPs, BiVO4/Bi NPs and BiVO4/Bi-Cucomposite photoanodes in a Na2SO4 electrolyte solution (at 1000 Hz)and (b) Semi-logarithmic dark J−V characteristics of the electrodes at forward bias region.

**Cyclic voltammograms (CV):**

For pristine BiVO4, the conduction band (CB) and the valance band (VB) positions were calculated using the following method:

E**red** = -0.873 V versus Ag/AgCl/KCl

Electrode potential of reference electrode = +0.197 V

E**red** versus NHE (normal hydrogen electrode)

E**red** = -0.873 V + 0.197 V = -0.676 V (NHE)

We converted V (volts) into eV (electron volts),

Therefore E**red** = -4.5 eV (0 V vs NHE) - (-0.68 V) = -3.82 eV (CB)

This value is equal to the CB position of BiVO4. Then the VB position of BiVO4 was obtained by the addition of the optical bandgap energy value to the CB energy.

E**red** = -3.82 eV + (−2.4 eV) = -6.12 eV (VB)



**Fig. S6** CV plots of bare BiVO4.