

Supplementary Information for
Understanding the synergistic effect of WO₃-BiVO₄
heterostructures by impedance spectroscopy

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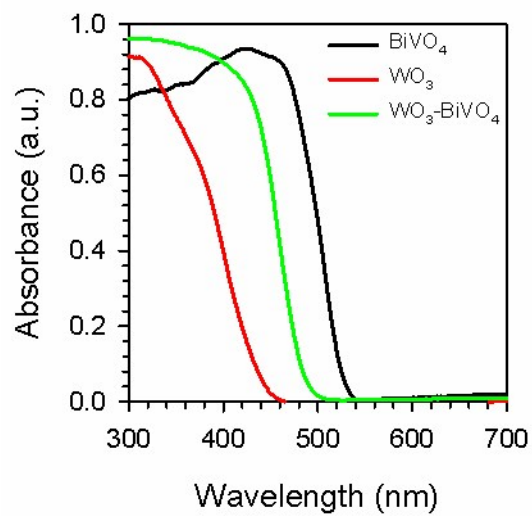


Figure S1.- Absorption spectra of the different structures WO₃, BiVO₄ and WO₃-BiVO₄.

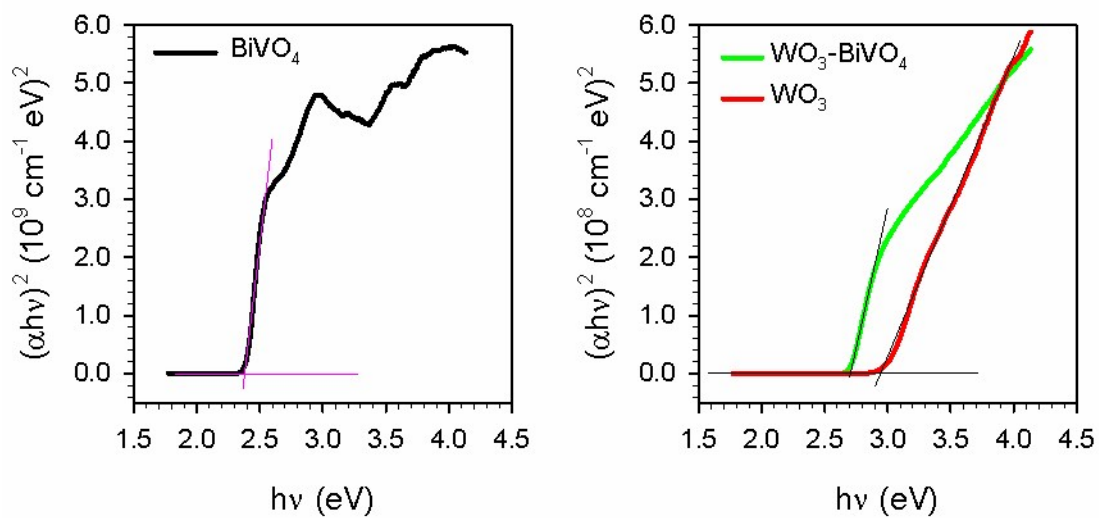


Figure S2. Tauc plots of the direct bandgap transition for the tested samples. The thickness employed for the calculation, extracted from SEM micrographs, is 1.7 μm for WO₃ and WO₃-BiVO₄, and 0.5 μm for BiVO₄.

S3. Calculation of charge separation efficiency (η_{cs}) and charge injection efficiency (η_{cat})

Calculation of charge separation efficiency (η_{cs}) and charge injection efficiency (η_{cat}) were carried out with equations (1) and (2) according to reference ¹, where j_{H_2O} is the photocurrent for water oxidation and j_{hs} is the photocurrent for the oxidation of the hole scavenger. The maximum current estimated from absorbance measurements (j_{abs}) was calculated from eq (3), where e is the electron charge, h is the Plank constant, c is the speed of light, λ is the wavelength, I_λ is the solar irradiance and A is the absorbance. Results for the estimated maximum photocurrent are showed in **Table S1**.

$$j_{H_2O} = j_{abs}\eta_{cs}\eta_{cat} \quad (1)$$

$$j_{hs} = j_{abs}\eta_{cs} \quad (2)$$

$$j_{abs} = \frac{e}{hc} \int \lambda I_\lambda (1 - 10^{-A}) \quad (3)$$

Table S1. Estimated maximum photocurrent values from the absorbance measurements in Figure S1 calculated from eq (3).

Material	j_{abs} (mA·cm ⁻²)
WO ₃	2.87
BiVO ₄	7.57
WO ₃ -BiVO ₄	5.50

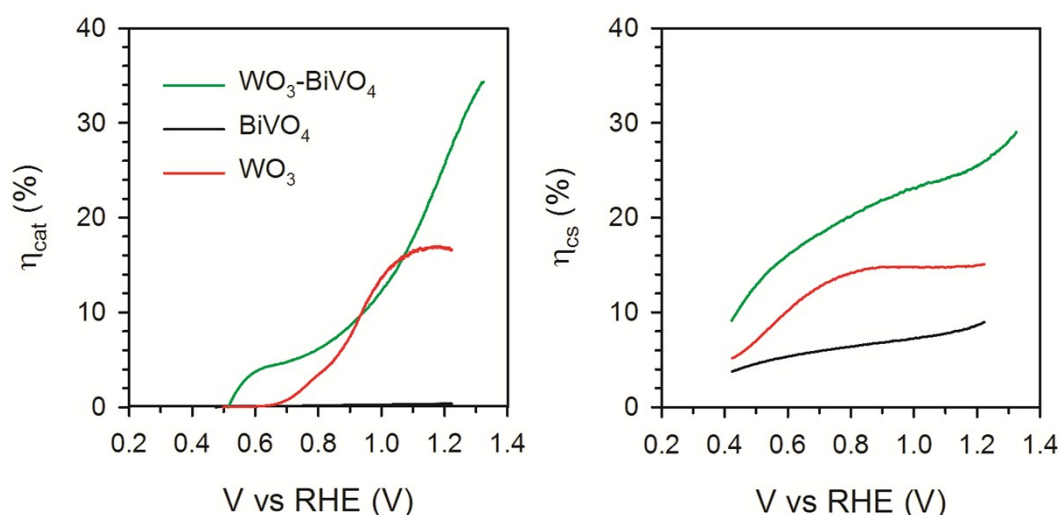


Figure S3. Charge injection efficiency (η_{cat}) and charge separation efficiency (η_{cs}) calculated for the three tested materials, WO₃, BiVO₄ and WO₃-BiVO₄.

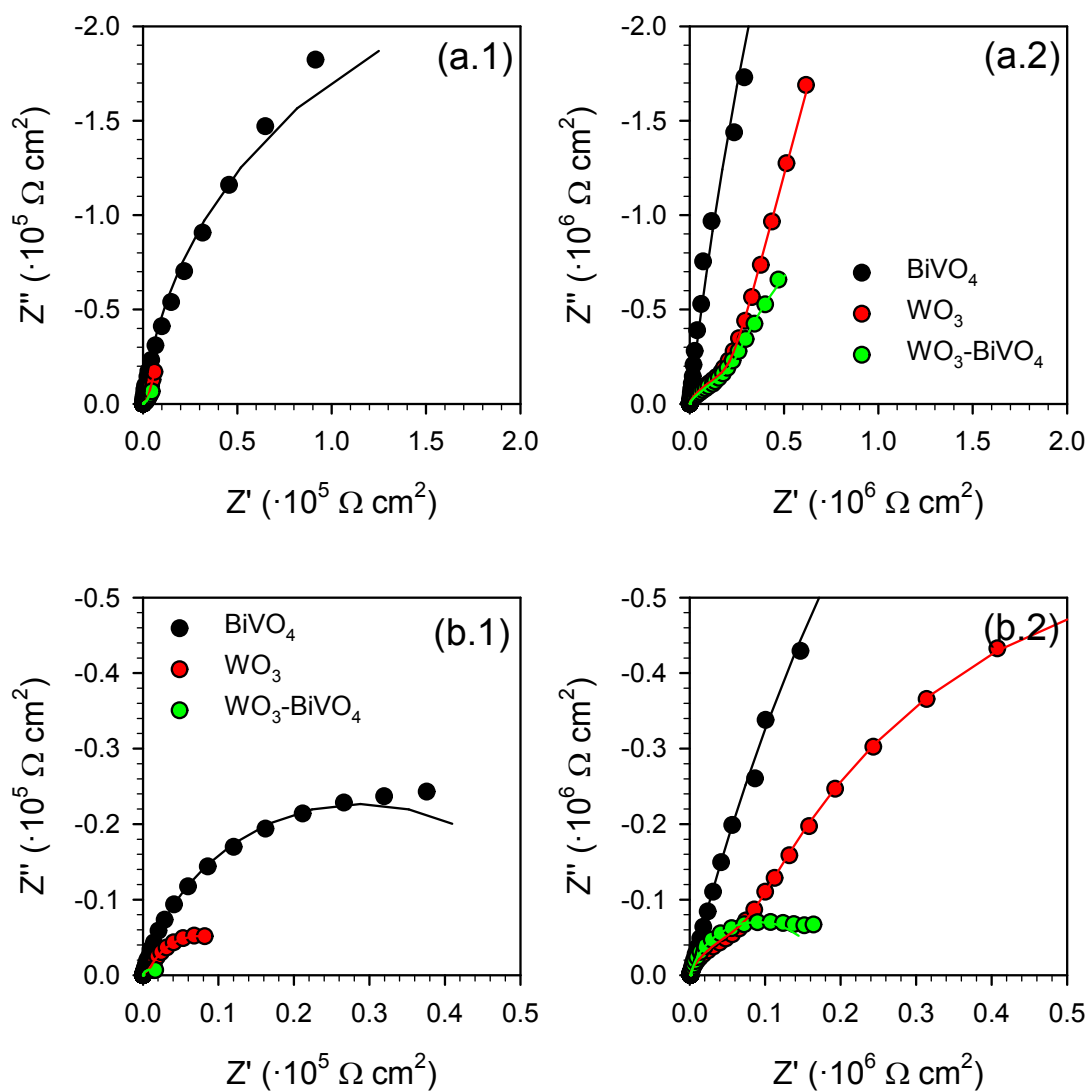


Figure S4. Nyquist plots for the tested samples obtained (a) in the dark, and (b) under illumination at 1.0 V vs. RHE. (a.2) and (b.2) correspond to a magnification of plots (a.1) and (b.1), respectively. Symbols: experimental data. Lines: fitting of the experimental data to the physical models described in Figure 2 of the main text.

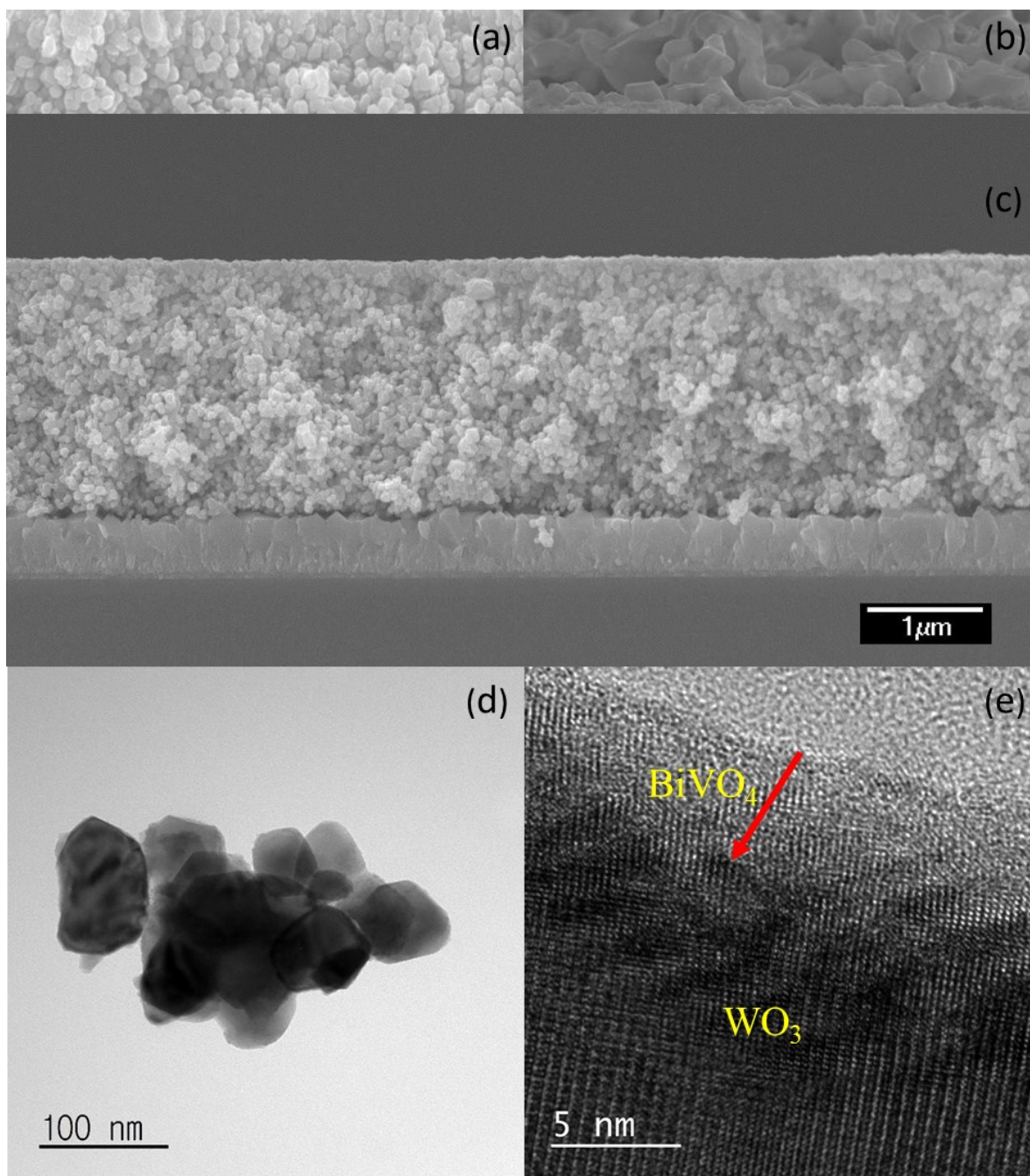


Figure S5. Morphologies of the studied photoanodes: (a) SEM image of WO_3 , (b) SEM image of BiVO_4 , (c) SEM image of $\text{WO}_3\text{-BiVO}_4$, (d) TEM image of $\text{WO}_3\text{-BiVO}_4$, and (e) HR-TEM image of $\text{WO}_3\text{-BiVO}_4$

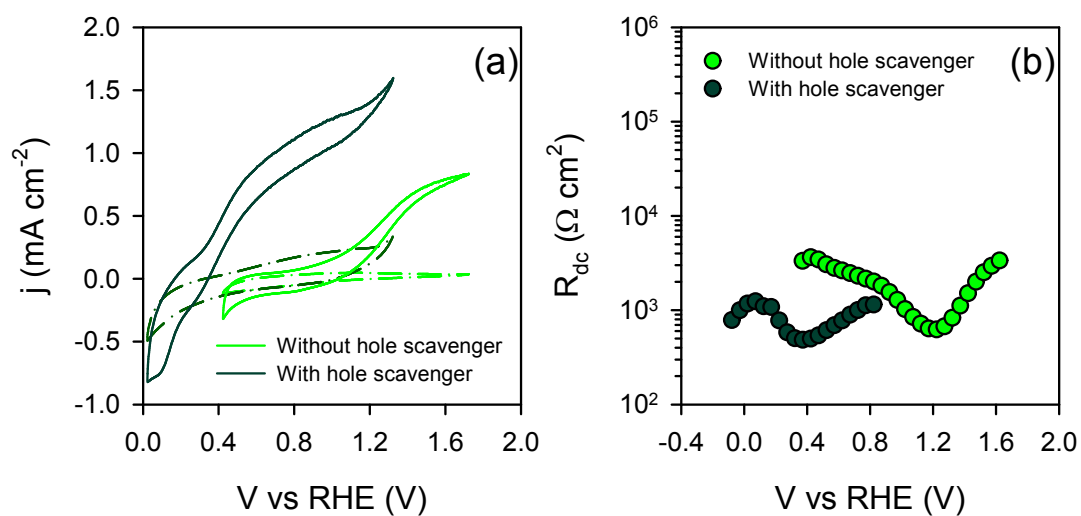


Figure S6. (a) j - V curves in dark (dashed lines) and under illumination at 100 mW·cm⁻² (solid lines); and (b) dc resistances, R_{dc} , extracted from fitting the impedance spectra obtained under illumination for the heterostructured WO₃/BiVO₄ photoanode, in 0.5 M Na₂SO₄ solution with and without hole scavenger (0.35 M Na₂SO₃).

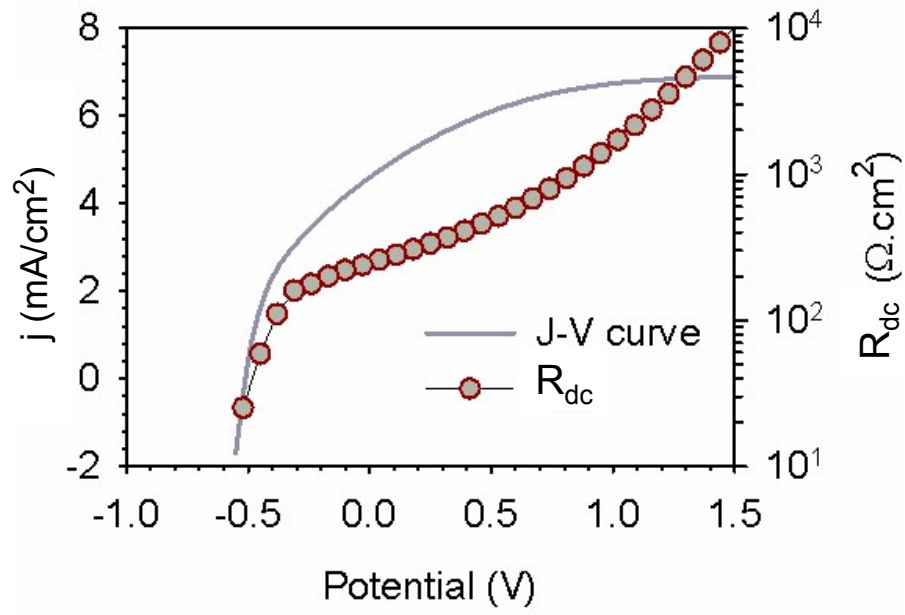


Figure S7. j - V curve and dc resistance for perfect selective contacts for both holes and electrons. In this case, the minimum of the charge transfer resistance is not observed. The values of the recombination rates are $B = 10^{-7} \text{ cm}^3/\text{s}$ and $S_n = S_p = 10^6 \text{ cm/s}$. The other parameters of this simulation are indicated in Table S2.

Parameters	Values	Unit
L	200	nm
$\kappa_B T$	26	m eV
$u_n = u_p$	10	cm ² /V
ϵ_r	10	
N_D	10 ¹⁶	cm ⁻³
N_A	0	
E_g	1	eV
$N_c = N_v$	10 ¹⁹	cm ⁻³
Φ_n	0.15	eV
Φ_p	0.6	eV
G_0	5×10 ²¹	cm ⁻³ ·s ⁻¹
α	10 ⁵	cm ⁻¹
S_p	10 ⁶	cm·s ⁻¹

Table S2 Values and units of the parameters used during the simulation process.

Model equations

These classical drift diffusion equations (continuity and Poisson equations) can be written as a system of 6 first order differential equations that govern the variations of 6 variables: the electron current \bar{j}_n , the hole current \bar{j}_p , the density of electrons \bar{n} and holes \bar{p} , the electrostatic potential $\bar{\phi}$ and the electric field \bar{F} :

$$\bar{j}_n = q\bar{n}u_n\bar{F} + qD_n \frac{\partial \bar{n}}{\partial x} \quad (4)$$

$$\bar{j}_p = q\bar{p}u_p\bar{F} - qD_p \frac{\partial \bar{p}}{\partial x} \quad (5)$$

$$\frac{1}{q} \frac{\partial \bar{j}_n}{\partial x} + G - U_r = 0 \quad (6)$$

$$-\frac{1}{q} \frac{\partial \bar{j}_p}{\partial x} + G - U_r = 0 \quad (7)$$

$$\frac{\partial \bar{F}}{\partial x} = \frac{q}{\varepsilon_0 \varepsilon_r} (\bar{p} - \bar{n} + N_D - N_A) \quad (8)$$

$$\bar{F} = -\frac{\partial \bar{\phi}}{\partial x} \quad (9)$$

Where G is the generation rate which is assumed to follow a Beer Lambert law ($G(x) = G_0 \exp(-\alpha x)$, where α is the absorption coefficient) and U_r is the band to band recombination rate defined as $U_r = B(\bar{n}\bar{p} - n_0 p_0)$, n_0 and p_0 being the equilibrium concentrations of electrons and holes:

$$n_0 = N_c e^{-\frac{\Phi_n}{k_B T}} \quad (10)$$

$$p_0 = N_v e^{-\frac{\Phi_p}{k_B T}} \quad (11)$$

N_c and N_v are the density of electrons at the bottom of the conduction band edge and the hole concentration at the top of the valence band edge, respectively. Φ_n and Φ_p are the electron and hole injection barrier, respectively. In addition, u_n and u_p are

the electron and hole's mobility, respectively, D_n and D_p are the electron and hole's diffusion coefficient, which are linked to the mobility by the Einstein relation $D_k = u_k k_B T / q$. N_D and N_A are the total density of ionized donors and acceptors, ϵ_0 and ϵ_r are the dielectric permittivity of the vacuum and the relative permittivity.

For the model presented in Figure 1 of the main text, we assume that at the semiconductor/metal interface ($x = 0$), the current of electrons can be written as:

$$\bar{j}_n(0) = qS_n(\bar{n}(L=0) - n_0) \quad (12)$$

We take as the reference for the potentials the electrostatic potential in $x = 0$:

$$\bar{\phi}(0) = 0 \quad (13)$$

We consider the metal to be a perfect electron selective contact (no hole current):

$$\bar{j}_p(0) = 0 \quad (14)$$

At the semiconductor/electrolyte interface, the conduction and valence band edges are pinned and the voltage drop at the Schottky barrier is linked to the electrostatic potential as: $V_{sc} = \bar{\phi}(L) - \bar{\phi}(0)$. V_{sc} and therefore $\bar{\phi}(L)$ is directly modulated by the applied voltage as:

$$\bar{\phi}(L) = V_{bi} + V \quad (15)$$

The hole current flowing through the semiconductor/electrolyte ($x = L$) follows the relation:

$$\bar{j}_p(L) = qS_p(\bar{p}(L) - p_0) \quad (16)$$

Finally, the electron current is assumed to be zero at this contact

$$\bar{j}_n(L) = 0 \quad (17)$$

Boundary conditions (12)–(17) allow one to obtain the complete solution to the system of equations (4)–(9).

References

1. H. Dotan, K. Sivula, M. Graetzel, A. Rothschild and S. C. Warren, *Energy & Environmental Science*, 2011, **4**, 958-964.