Supplementary Information (SI) for Nanoscale.

Microwave-assisted synthesis of ZnO/$BiNbO_4$ heterojunctions for enhanced hydrogen production

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SEM image

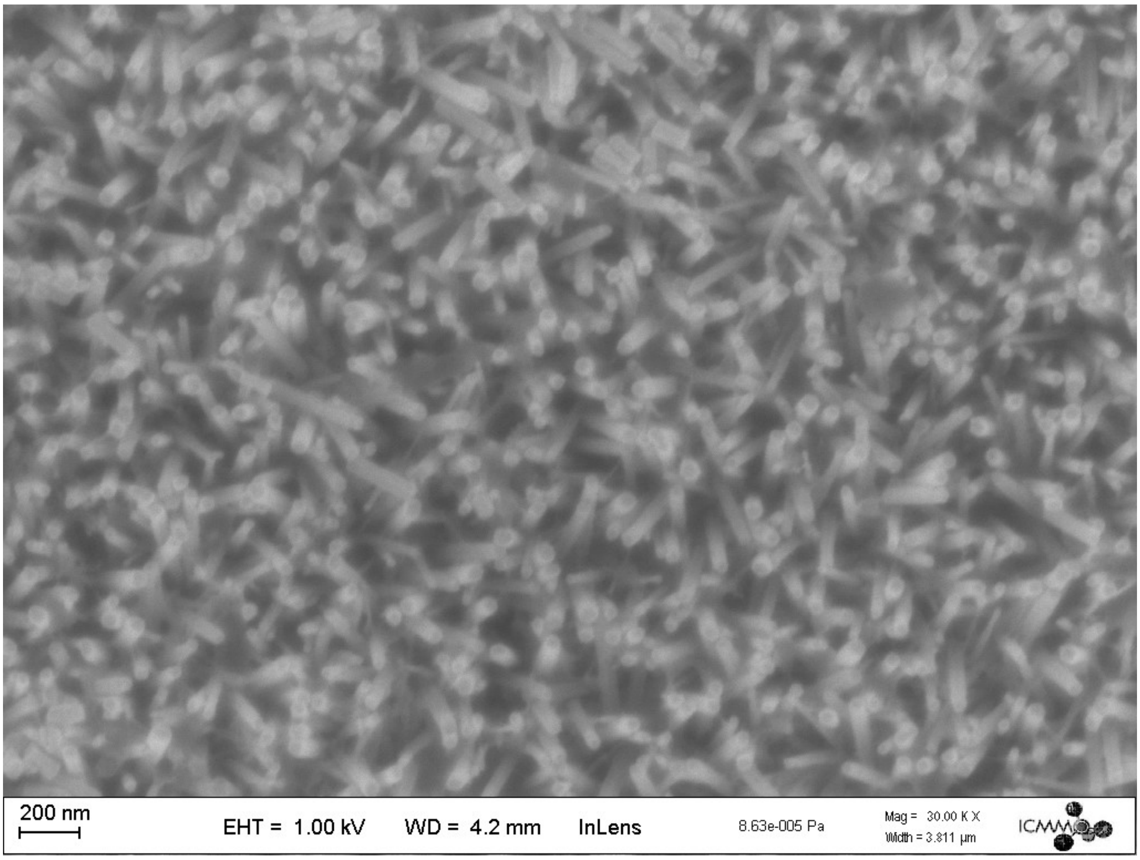

Figure S1. SEM image of ZnO film.

HRTEM investigation

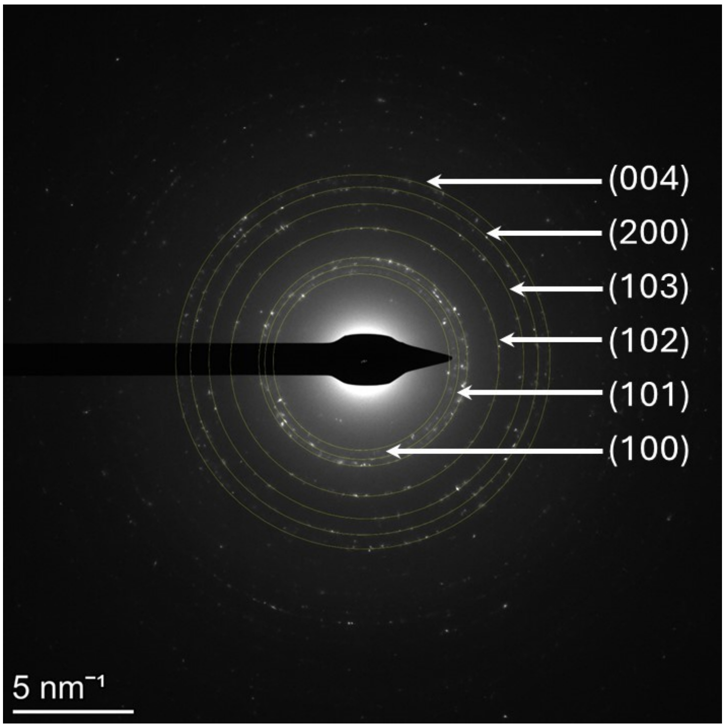

Figure S2. Pattern diffraction obtained from the selected area electron diffraction (SAED) of ZnO.

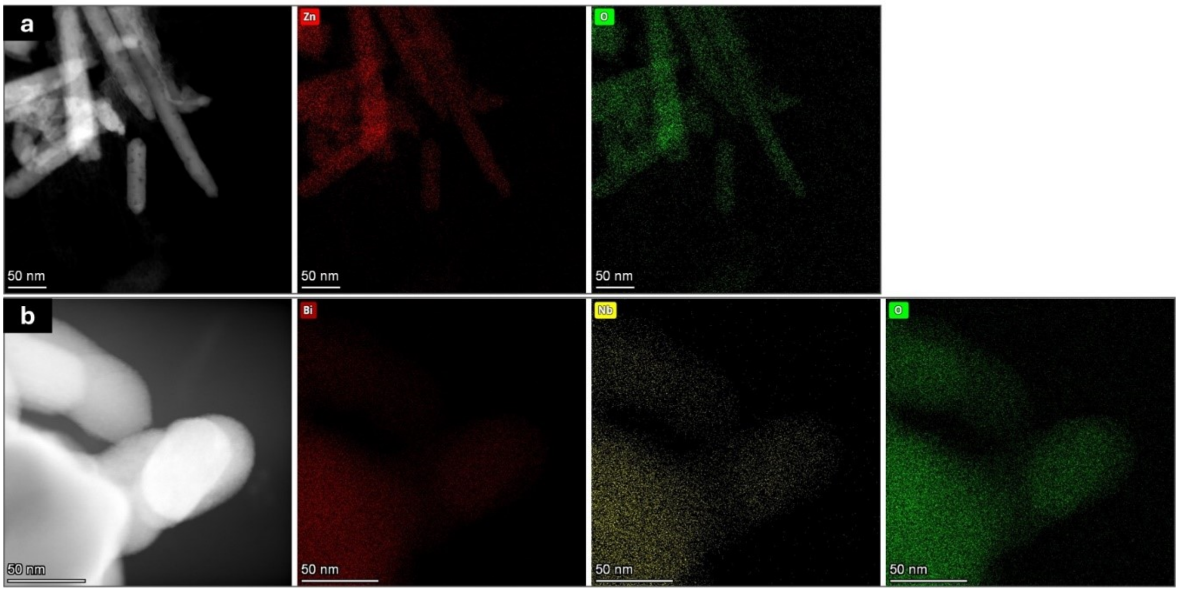

Figure S3. STEM images and elemental mapping of samples a) ZnO and b) $BiNbO_4$.

XPS survey

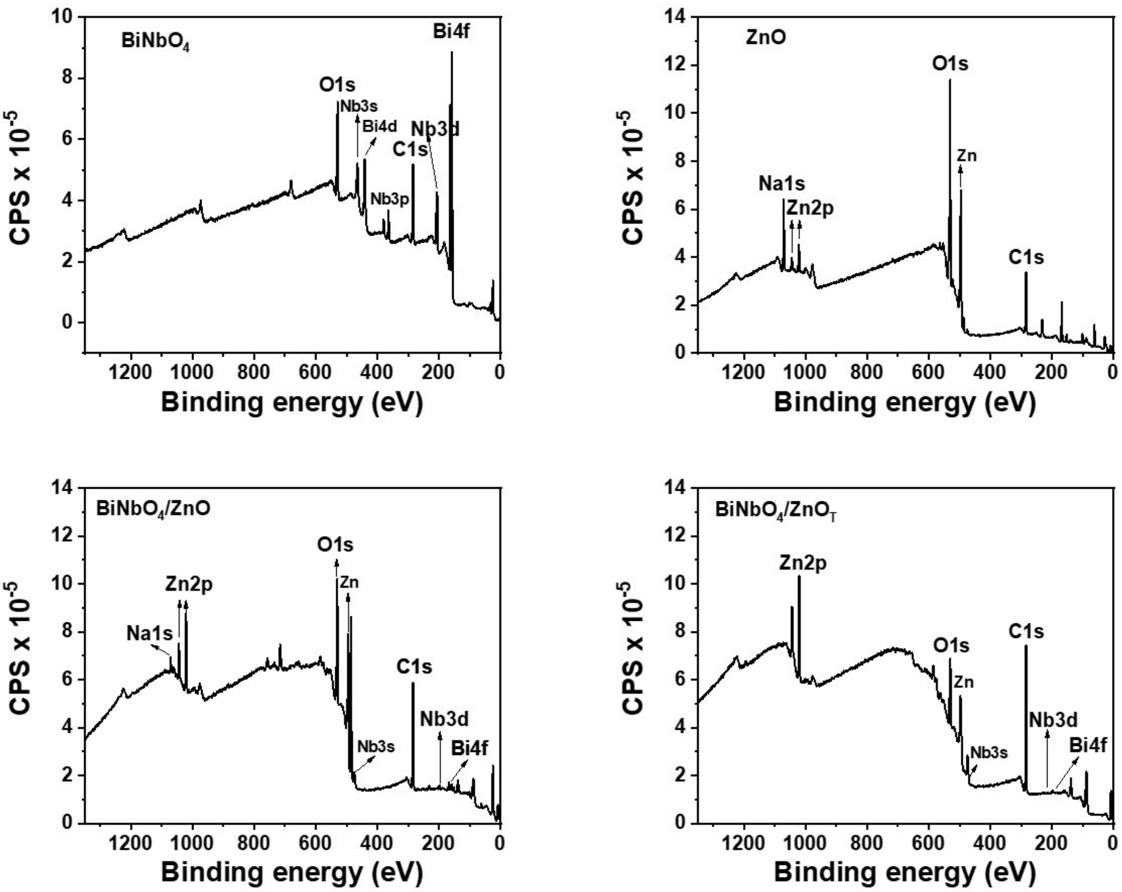

Figure S4. XPS survey spectra of ZnO, $BiNbO_4$, $BiNbO_4$/ZnO and $BiNbO_4$/ZnO_T samples.

UPS analysis

The procedure for calculating the valence band (VB) and the conduction band (CB) obtained from the UPS spectrum is described below.[1]

First the work function (φ) was calculated using the equation S1:

$$\varphi = h\nu - E_{SEO} \quad \text{Equation S1}$$

where, $h\nu$ is 21.22 eV and represents the energy of the monochromatic ionizing light, while $E_{SEO}$is the secondary electron onset, obtained from the linear extrapolation of the UPS spectra.

Then, the Fermi level (E_f) was obtained usinf equation S2:

$$E_f = -\varphi \quad \text{Equation S2}$$

The position of the VBM was calculated from equation S2:

$$E_{VBM} = E_f - X \quad \text{Equation S3}$$

where X is obtained from the extrapolation of the onsets in the UPS spectrum. Following the conduction band minimum potential (E_{CBM}) was obtained from equation S4:

$$E_{CBM} = E_{VBM} + E_g \quad \text{Equation S4}$$

where E_g is the bandgap energy obtained by tauc plots.

As a result E_f, E_{VBM} and E_{CBM} values refer to the vacuum energy (eV vs. Vacuum level). The vacuum energy (E_{VAC}) in electronvolt can be converted to E (V vs. RHE - reversible hydrogen electrode) using the equation S5:

$$E_{RHE} = -E_{VAC} - 4.44 \quad \text{Equation S5}$$

The value of the potential of RHE equals the normal hydrogen electrode (NHE) at pH = 0.

The UPS spectra used for the calculations made for $BiNbO_4/ZnO$ and $BiNbO_4/ZnO_T$ are shown in Figure S5.

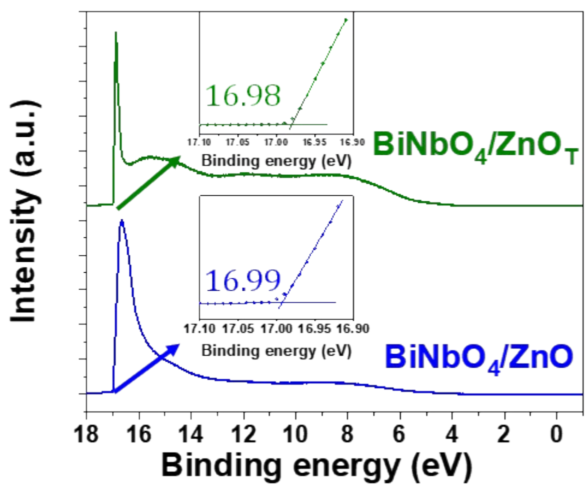

Figure S5. Ultraviolet photoelectron spectra (He-I) of $BiNbO_4/ZnO$ and $BiNbO_4/ZnO_T$ samples.

All the calculated values are displayed in Table S1.

Table S1. Parameter extracted from UPS, VB XPS and DRS spectra of ZnO, $BiNbO_4$, $BiNbO_4$/ZnO and $BiNbO_4$/ZnO_T.

Material	E_{SEO}**(eV)**	φ **(eV)**	E_f**(eV)**	X **(eV)**	E_{VBM} **(eV)**	E_g **(eV)**	E_{CBM} **(eV)**	E_{VBM} **(V *vs.* NHE)**	E_{CBM}**(V *vs.* NHE)**
ZnO	17.49	3.73	-3.73	3.76	-7.49	3.26	-4.23	3.05	-0.21
$BiNbO_4$	16.55	4.67	-4.67	3.69	-8.36	3.22	-5.14	3.92	0.70
$BiNbO_4$/ZnO	16.99	4.23	-4.23	3.66	-7.89	3.24	-4.65	3.45	0.21
$BiNbO_4$/ZnO_T	16.98	4.24	-4.24	3.88	-8.12	3.19	-4,93	3.68	0.49

Band gap calculation

Band gap energy of the ZnO, $BiNbO_4$, $BiNbO_4$/ZnO and $BiNbO_4$/ZnO_T films was estimated using the Kubelka Munk Function (Equation S6) from DRS data (Figure 6c):

$$F(R) = K/S \qquad \text{Equation S6}$$

where K is the molar absorption coefficient (Equation S7) and S is the scattering factor (Equation S8):

$$K = (1 - R)^2 \qquad \text{Equation S7}$$

$$S = 2R \qquad \text{Equation S8}$$

R is the reflectance of the material (Equation S9):

$$R = \%R/100 \qquad \text{Equation S9}$$

The combination of Equations S7, S8 and S9 Equation S10:

$$F(R) = (1 - R)^2/2R \qquad \text{Equation S10}$$

Mott-Schottky Plots

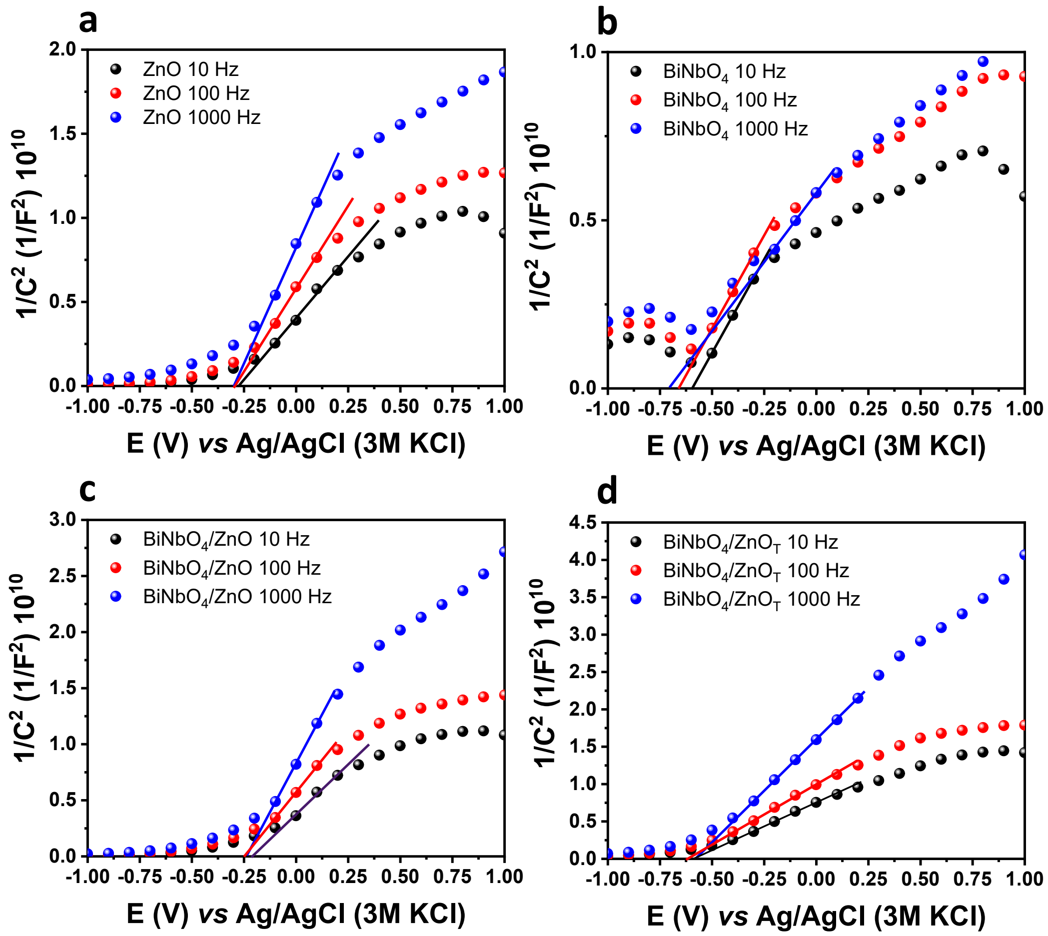

Figure S6. Mott-Schottky plots of ZnO (a), $BiNbO_4$ (b), $BiNbO_4/ZnO$ (c) and $BiNbO_4/ZnO_T$ (d) samples collected at different frequencies.

Table S2. Calculated slope, intercept and V_{fb} values from the linear fit of the Mott-Schottky plots obtained at 10, 100 and 1000 Hz. Reference electrode Ag/AgCl 3M KCl.

Material	10 Hz			100 Hz			1000Hz		
	Slope	Intercept	V_{fb}(V)	Slope	Intercept	V_{fb}(V)	Slope	Intercept	V_{fb}(V)
ZnO	4,04E13	1,48+15	-0,27	5,76E14	1,97E15	-0,29	8,26E14	2,77E15	-0,30
$BiNbO_4$	6,56E14	1,10E15	-0,60	7,36E14	1,12E15	-0,66	5,82E14	8,43E14	-0,69
$BiNbO_4/ZnO$	3,74E14	1,80E15	-0,21	5,75E14	2,33E15	-0,25	8,32E14	3,50E15	-0,24
$BiNbO_4/ZnO_T$	7,49E14	1,25E15	-0,60	1,00E15	1,61E15	-0,62	1,60E14	2,72E14	-0,59

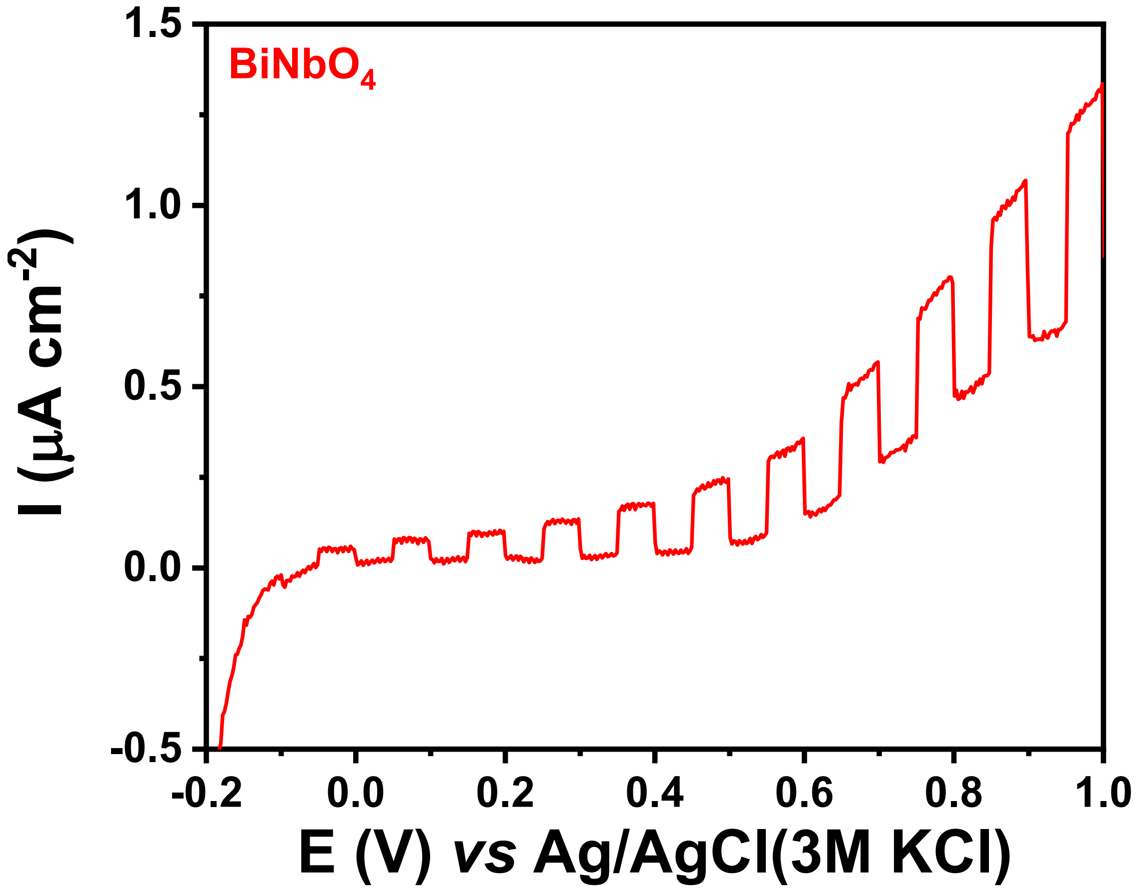

Figure S7. Chopped-light linear sweep voltammogram acquired using $BiNbO_4$ film as the working electrode. Ag/AgCl (KCl 3M) was used as a reference, and a Pt wire as a counter electrode. An aqueous solution of 0.01 M Na_2SO_4 was used as electrolyte. The scan rate was 50 mV s^{-1}.

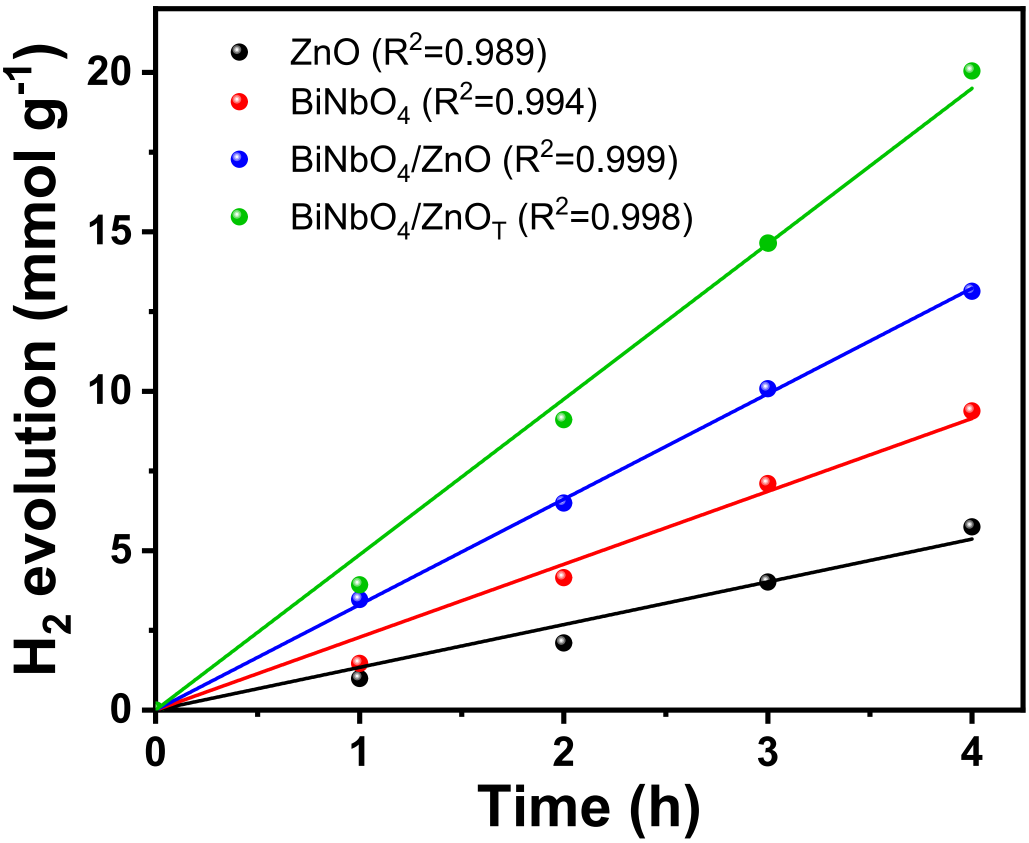

Figure S8. H_2 evolution of ZnO, $BiNbO_4$, $BiNbO_4$/ZnO and $BiNbO_4/ZnO_T$ films under UV light.

1. B. Su, H. Huang, Z. Ding, M. B. J. Roeffaers, S. Wang and J. Long, *Journal of Materials Science & Technology*, 2022, **124**, 164-170.