Synthesis of Ni-based co-catalyst functionalized W:BiVO₄ nanofibers for solar water oxidation

Electronic Supplementary Information

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11 Experimental Details

Synthesis of W:BiVO₄ NFs: All chemicals were purchased and used as received without 12 further purification. The precursor solution (weight ratio of precursor salts : polymer = 3 : 1) 13 for electrospinning was prepared by dissolving certain amounts of Bi(NO₃)₃·5H₂O (98%, 14 JUNSEI), VO(AcAc)₂ (98%, Sigma-Aldrich), and W(OC₂H₅)₅ (95%, Alfa Aesar), but total 15 amount of precursors was fixed with 3 g, in a 7.5 g of N,N-dimethylformamide (DMF, 99.8%, 16 Sigma-Aldrich). Then, 1 g of polymers, such as a polyvinylpyrrolidone (PVP, M_w) 17 ~1,300,000), a polyvinyl acetate (PVAc, M_w ~500,000), and a mixture of PVP/PVAc with a 18 ratio of 1:1 were added into the solution. After vigorous stirring at 500 rpm for 12 h at room 19 temperature, homogeneously mixed dark green solution was obtained, and the solution was 20 injected into the syringe for the electrospinning process. A high voltage of 17 kV was applied 21 between the needle (25 gauge) and the drum-type collector using a high-voltage DC power 22 supply. The feeding rate of solution was fixed with 0.08 mL min⁻¹, then the elongated 23 precursors/polymers composited fibers were collected on the rolling stainless steel substrate. 24 Subsequently, the collected fibers were calcined at 450 °C in air for 1 h (5 °C min⁻¹) using a 25 muffle furnace (Neytech, Vulcan furnace 3-550). After calcination, naturally cooled yellow 26 residues, W:BiVO₄ NFs, were obtained and directly used as experimental samples. 27

28 *Preparation of W:BiVO*₄ *particles:* W:BiVO₄ particles were synthesized by solid-state 29 reaction process and used as reference samples. A stoichiometric mixture of Bi_2O_3 , V_2O_5 and 1 WO₃ was ground and mixed vigorously in an agate mortar for 20 min. The well-mixed
2 powders were preheated at 400 °C for 2 h, and then calcined at 600 °C for 5 h. The obtained
3 yellow powders were ball-milled with 300 rpm for 24 h to obtain W:BiVO₄ particles.

Synthesis of Ni and Pt NPs: Ni NPs were synthesized by a modified polyol method. 0.1 g of 4 $Ni(NO_3)_2 \cdot 6H_2O$ and the same amount of PVP (0.1 g, $M_w \sim 10,000$) as a protective agent were 5 dissolved in 20 mL of ethylene glycol (EG) solution in 125 mL three neck flask. The 6 Ni/PVP-EG solution was maintained under magnetic stirring until the homogeneous 7 dissolution of the precursor and PVP at 140 °C in an oil bath. 0.36 g of NaBH₄ (96%, Sigma-8 Aldrich) as a reducing agent was added during stirring. The pale green colored solution 9 immediately changed into a strong dark colored solution after NaBH₄ addition. The system 10 was maintained under magnetic stirring at 140 °C for 2 h. To isolate the Ni NPs from the 11 solvent, the mixed solution was centrifuged at 2,000 rpm for 10 min, and consequently the 12 supernatant was discarded and washed with ethanol for three times. The obtained black 13 colloidal solution dispersed in ethanol was directly used as the Ni NPs additive source. Pt 14 NPs were also synthesized using the polvol method and the obtained Pt NPs were shown in 15 Figure S6. 16

Preparation of Ni@NiO, NiO and Pt NPs-loaded W:BiVO4 NFs: Decoration of Ni NPs on 17 W:BiVO₄ NFs was carried out with different amount of Ni colloidal solution. W:BiVO₄ NFs 18 were dispersed in ethanol with magnetic stirring for 20 min and sonication for 5 min. After 19 then, certain amounts of Ni colloidal solution (0.01, 0.1, and 1 wt% Ni) were added to the 20 W:BiVO₄ NFs dispersed ethanol solution. After stirring for 30 min, the solution was 21 maintained in the oven at 80 °C to evaporate the solvent for overnight. The dried mixture of 22 Ni and W:BiVO₄ NFs was annealed at 300 °C for 2 h in an Ar filled tube furnace to minimize 23 the oxidation of metallic Ni. Then, partially oxidized Ni@NiO-loaded W:BiVO₄ NFs were 24 obtained. As a reference, NiO-loaded W:BiVO₄ NFs were also prepared with similar 25

procedure of Ni@NiO/W:BiVO₄ NFs, but they were annealed at 450 °C for 2 h in air to make
 fully oxidized NiO NPs. Pt-loaded W:BiVO₄ NFs were also prepared by similar process with
 Ni@NiO/W:BiVO₄ NFs as mentioned above.

4 *Water Oxidation Test:* The water oxidation reaction was conducted in 60 mL vial containing 5 30 mL of deionized water with 255 mg of silver nitrate as a sacrificial electron scavenger and 6 30 mg of the photocatalyst samples. The reaction solution was irradiated using a xenon lamp 7 (450 W) with a 420 nm cut-off filter and purged with N₂ (99.999%) gas as a carrier gas. The 8 evolved O₂ gas was continuously monitored using a series 3500 Trace Oxygen Transmitter 9 (Alpha Omega Instruments Co., USA). External quantum efficiency (η) was calculated using 10 the equation below:

$\eta = 100 \times (4 \times \# \text{ of evolved O}_2) / (\# \text{ of incident photons}) (1)$

12 *Photocurrent Measurement:* Photo-electrodes were prepared by drop casting of each sample 13 (500 μ g) on FTO glass (1 x 1 cm²). Photo-electrodes were cured at 50 °C for 10 hr to attach 14 samples on FTO glass. Photocurrent response experiments were conducted with prepared 15 photo-electrodes, a platinum wire (as a counter electrode), Ag/AgCl reference electrode, and 16 NaSO₄ (0.5 M) solution using WMPG 1000 potentiostat (WonATech, Korea). An applied 17 potential for photo-electrodes against Ag/AgCl reference electrode was set to 0.5 V.

Materials Characterization: The microstructures of the prepared samples were observed 18 using a FEI Magellan XHR 400L scanning electron microscope (FEI Company, USA) and a 19 Tecnai F30 S-Twin transmission electron microscope (FEI Company, USA). The element 20 distribution was investigated using EDS and STEM mapping. The crystalline phase of the 21 samples was analyzed by using a D/MAX-RB (12KW) X-ray diffractometer (RIGAKU Co., 22 Japan) and Sigma-Probe X-ray photoelectron spectroscopy (Thermo VG Scientific, UK). The 23 mass change of a sample as a function of temperature and time in the isothermal mode was 24 measured using a TG209 F3 thermogravimetry analyzer (NETZSCH, Germany). The surface 25

- 1 area of the samples was measured by using the Brunauer-Emmett-Teller (BET) method with
- 2 an ASAP 2020 surface area analyzer (Micromeritics, USA).



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Figure S1. Schematic illustration of Ni@NiO/W:BiVO₄ nanofibers fabrication process. (i) 4 $(Bi(NO_3)_35H_2O, VO(AcAc)_2,$ Metal salts and $W(OC_2H_5)_5$) and two polymers 5 (polyvinylpyrrolidone (PVP, M_w~1,300,000) and polyvinyl acetate (PVAc, M_w~500,000)) 6 dissolved in N,N-dimethylformamide (DMF) solution were electrospun. By applying high 7 voltage between needle and collector, one dimensional (1-D), elongated fibers were ejected. 8 (ii) Collected as-spun fibers were calcined at 450 °C for 1 h and yellow W:BiVO₄ NFs were 9 obtained. (iii) To integrate Ni NPs and W:BiVO₄ NFs, the W:BiVO₄ NFs and as-prepared Ni 10 NPs were put together in ethanol solution and stirred to get homogeneously mixed sample, 11 followed by drying at 80 °C overnight. (iv) Finally, the collected remnants were annealed at 12 300 °C in Ar-filled tube furnace for 2 h to provide tight binding between Ni NPs and 13 W:BiVO₄ NFs. 14





2 Figure S2. SEM images of as-spun fibers using electrospinning from the solution containing Bi/V/W precursors and (a) PVP, (b) PVAc, and (c) PVP/PVAc mixed polymers with the 3 weight ratio of 1:1. SEM images of calcined W:BiVO₄ NFs prepared from each (a), (b), and 4 (c) as-spun fiber. Each as-spun fiber has a similar morphology, a long stretched shape with 5 smooth surface. (d) SEM image of W:BiVO₄ synthesized only with PVP. The nanofibers 6 consist of large grains with a smooth surface and show a dense structure without any pores. (e) 7 W:BiVO₄ NFs prepared only with PVAc exhibit numerous pores on the surface of the 8 irregular structure. (f) W:BiVO₄ NFs prepared from PVP/PVAc mixed polymer solution 9 show one-dimensional structure with high porosity and stable 1-D morphology as compared 10 with PVP and PVAc-driven W: BiVO₄ NFs. 11



Figure S3. Energy-dispersive X-ray spectroscopy (EDS) data of W:BiVO₄ NFs (1 at% W
 substituting for V).



Figure S4. SEM images of (a) the as-spun Bi, V, O, and W precursors/PVP composite fibers,
and the calcined W:BiVO₄ NFs at (b) 350, (c) 450, (d) 550, (e) 650 and (f) 750 °C for 1h.



2 Figure S5. The relation of BET surface area (black dots) and crystalline size (blue dots) of

3 W:BiVO₄ NFs synthesized at different calcination temperature. The crystalline size was

4 calculated by Scherrer's equation.

1 Table S1. The calcination temperature, crystalline size, and BET surface area of W:BiVO₄

2 NFs and particles.

Sample	Calcination temperature	Synthetic method	Crystalline size (nm)	BET surface area (m ² g ⁻¹)
W:BiVO ₄ NFs	350 °C for 1h	Electrospinning 61.23		18.95
	350 °C for 1h	Electrospinning 77.82		13.66
	550 °C for 1h	Electrospinning	101.30	10.81
	650 °C for 1h	Electrospinning	126.02	6.35
	750 °C for 1h	Electrospinning	173.83	3.30
W:BiVO ₄ particles	400 °C for 2 h and 600 °C for 5h	Solid-state reaction	245.68	2.88

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2 Figure S6. X-ray diffraction patterns of pristine, 0.01, 0.1, and 1 wt% Ni@NiO-loaded

3 W:BiVO₄ NFs.



Figure S7. XPS survey scan of W:BiVO₄ NFs, Ni@NiO/W:BiVO₄ NFs, and NiO/W:BiVO₄
 NFs.



2 Figure S8. Plots of cyclic voltammetry (CV) curves of Ni@NiO/W:BiVO₄ NFs for 0, 30, 60,

- 3 90, and 120 min. (Scan rate: 20 mV s⁻¹, in three electrodes system, reference electrode was
- 4 Ag/AgCl). For conversion of the obtained potential (vs. Ag/AgCl) to RHE (NHE at pH = 0),
- 5 the equation below was used. $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E_{Ag/AgCl}^0 (E_{Ag/AgCl}^0 = +0.199 \text{V})$



- 2 Figure S9. a) TEM images of platinum nanoparticles (Pt NPs) (inset image shows ring
- 3 pattern of Pt NPs and b) lattice fringes of Pt NPs. c) TEM images of 0.1 wt% Pt NPs-loaded
- $4 \quad W:BiVO_4 \ NFs \ (Pt/W:BiVO_4 \ NFs) \ and \ d) \ lattice \ fringes \ of \ Pt/W:BiVO_4 \ NFs.$



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- 2 **Figure S10.** (a) UV-visible diffuse-reflectance spectra, (b) Tauc plots of $[hv \cdot F(R_{\infty})]^2$ versus
- 3 photon energy, and (c) visual photographs of pristine, 0.01, 0.1, and 1 wt% Ni@NiO-loaded
 4 W:BiVO₄



Figure S11. (a) SEM image of as-prepared W:BiVO₄ particles synthesized by solid-state reaction process. (b) SEM image of ball-milled W:BiVO₄ particles, which have a diameter range of 50-200 nm. (c) XRD pattern and (d) UV-visible diffuse-reflectance spectra of W:BiVO₄ particles. The XRD pattern of W:BiVO₄ particles shows monoclinic-scheelite phased BiVO₄ corresponding to PDF#14-0688 (BiVO₄), and the calculated band gap from Tauc plot is 2.41 eV.





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Figure S12. (a) The time courses of O₂ evolution under visible light ($\lambda > 420$ nm) irradiation 2 for 1.5 h. (b) The plot of W contents (at%) in W:BiVO₄ NFs versus evolved O₂. (c) The XRD 3 4 patterns of W:BiV_{1-x} W_xO_4 NFs (x = 0, 0.1, 0.5, 1, 2, 4, and 8) and d) enlarged patterns of (c) in the ranges between 28 and 36°. The photocatalytic activity for O₂ evolution increased up to 5 the 1 at% of W dopant concentration in BiVO₄ NFs. The maximum amount of evolved O₂ 6 was 3.51 µmol for 1.5 h with 1 at% W:BiVO₄ NFs, which is 2.1 times higher than that of 7 pristine BiVO₄ NFs (1.61 µmol). This can be explained by the electronic conductivity of 8 BiVO₄. The conductivity of a material, σ , is a function of the carrier concentration and the 9 carrier mobility μ , as shown in Equation: 10

$$\sigma = ne\mu_e + pe\mu_h pprox ne\mu_e$$

12 in which e is the elementary charge, and n and p are the electron and hole concentrations, 13 respectively. As $BiVO_4$ is an n-type semiconductor, the contribution of electrons is 14 significant whereas that of holes can be negligible. The effect of W doping incorporated in 15 pristine $BiVO_4$ is illustrated by the defect chemistry, written in the Krçger–Vink notation: 16

$$2WO_{3} + Bi_{2}O_{3} \xrightarrow{BiVO_{4}} 2Bi_{Bi}^{\times} + 2W_{V}^{\bullet} + 8O_{0}^{\times} + \frac{1}{2}O_{2}(g) + 2e^{-1}$$

In the case of 1:1 stoichiometry of Bi and (W+V) sites, which can be denoted as Bi $(V_1$. 1 $_{x}W_{x}O_{4}$, one can expect that additional electrons increase the conductivity of BiVO₄. 2 Furthermore, the higher formal electron charge of W⁶⁺ compared to V⁵⁺ produces a local 3 internal-field, resulting in the efficient charge separation, which increase the lifetime of the 4 When the dopant concentration increased more than 1 at %, on the other charge carriers. 5 hand, the amount of evolved O₂ is found to deteriorate, and the amount of evolved O₂ on 8 at % 6 W:BiVO₄ NFs even less than that of pristine BiVO₄ NFs. This result came from the 7 degradation of monoclinic-scheelite structure of BiVO₄ induced by the different ionic radius 8 (r_i) between host ($r_i V^{5+} = 68$ pm) and dopant ($r_i W^{6+} = 74$ pm). As shown in Fig. S10b, the 9 gradual peak shift near 28.4°, corresponding to (121) plane of monoclinic-scheelite phased 10 BiVO₄, occurred as the dopant concentration increased. However, the excessive dopants in 11 host materials produce the severe lattice deformation, resulting in broadening the XRD peaks, 12 especially in {200} family related peaks of monoclinic-scheelite phased BiVO₄ around 35°, 13 and finally in degenerating of water oxidation properties. 14 15 16 17 18 19 20

1 **Table S2**. Co-catalyst loading, band gap, and the average amount of evolved O_2 for the 2 prepared samples. Photocatalytic water oxidation test of prepared samples was carried out 3 from an aqueous solution containing silver nitrate (50 mol L⁻¹) as an electron acceptor under 4 visible light irradiation. 30 mg of photocatalyst samples^a was dispersed in a solution (30 mL) 5 with magnetic stirring in a gas-closed circulation system during the water oxidation reaction 6 for 3 h. The average amount of evolved O_2^{b} was obtained from three independent 7 measurements.

Host catalyst ^a	Co-catalyst [wt% to W:BiVO ₄]	Band gap (eV)	The average amount of evolved O ₂ [standard deviation] (μmol) ^b
W:BiVO4 NFs	Ni@NiO [10]	2.52	14.44 [0.274]
	Ni@NiO [1]	2.52	15.28 [0.125]
	Ni@NiO [0.2]	2.52	16.14 [0.384]
	Ni@NiO [0.1]	2.52	19.34 [0.326]
	Ni@NiO [0.01]	2.52	16.25 [0.189]
	NiO [0.1]	2.53	7.32 [0.296]
	Pt [10]	-	4.44 [0.458]
	Pt [1]	-	7.39 [0.391]
	Pt [0.2]	-	6.73 [0.127]
	Pt [0.1]	-	7.51 [0.413]
	Pt [0.01]	-	6.24 [0.170]
	-	2.53	5.59 [0.512]
W:BiVO ₄ particles	-	2.41	2.95 [0.235]

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2 Figure S13. The O₂ evolution rate of Ni@NiO or Pt/W:BiVO₄ NFs versus the mole fraction
3 of Ni@NiO (blue square) or Pt (red square).

Table S3. Co-catalysts, system, the amount of evolved O₂, and reaction time, turn over
 frequency (TOF) in photocatalytic water oxidation with BiVO₄ based materials.

Materials	System	Evolved O ₂ (µmol)	Time (h)	Turn over frequency 4·[O ₂]/[catalyst]·time	Reference
Co-Pi/BiVO ₄	D	~140	3	0.302	12(f)
CoO _x /BiVO ₄	Potassium phosphate	~38		0.082	
IrO _x /BiVO ₄	(pH 7) + NaIO	~32		0.069	
RuO _x /BiVO ₄	ThatO3	~36		0.078	
Ammonia co- precipitated BiVO ₄	AgNO ₃	26 μmol/h		0.131	7(d)
Ni@NiO/W:BiVO ₄ NFs	AgNO ₃	10	1	0.432	This work



2 **Figure S14.** Time courses of O_2 evolution of W:BiVO₄ particles, W:BiVO₄ NFs, and 3 0.1Ni@NiO/W:BiVO₄ NFs under blue light emitting diode ($\lambda \sim 450$ nm) irradiation for 20 4 min for the calculation of the external quantum efficiency.