Electronic Supporting Information (ESI)

Pulse electrosynthesized nanoporous nickel oxyhydroxide-borate thin film in electro- and

photoelectro-reforming of methanol for selective production of formate

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Experimental Section

General consideration. Starting materials for the synthetic part of the work were purchased from commercial suppliers and of the highest available purity for the analytical work. Single-electrode type screen-printed carbon electrodes (SPCE, Zensor R&D, Taiwan), with a geometric surface area of 0.071 cm^2 , were used as received. Flourine-doped tin oxide (FTO) coated glass (sheet resistance 7 ohm sq–1, TEC GlassTM 7) substrates ($1.0 \times 3.0 \text{ cm}^2$) were cleaned with an ammonia-hydrogen peroxide-deionized water mixture (volume ratio: 1:1:5) at 70 °C for 30 min, after which the FTO substrates were dried at room temperature under nitrogen purge. Methanol stock solution (0.5 M) was prepared before each experiment by direct dilution of methanol (99.9%, Aencore Chemical Co., LTD) with electrolyte solutions. Deionized water (DIW) was used throughout the work.

Preparation of the SPCE|**NiBi electrode.** NiOOH-borate thin film was deposited onto the SPCE by electrodeposition in 0.1 M borate buffer (pH 9.2) containing 0.5 mM nickel sulfate. The electrodeposition of NiBi was carried out using a CHI 660E electrochemical workstation (CH Instruments, Inc., USA) with a conventional three-electrode electrochemical cell with SPCE as the working electrode, Pt foil (exposed area 4.0 cm²) as counter electrode, and Hg/HgO (1 M NaOH) as reference electrode. Both modes of constant current (CED) and pulse current electrodeposition (PED) were used for the electrodeposition of NiBi, and the resultant electrodes are designated as SPCE|NiBi_(CED) and SPCE|NiBi_(PED), respectively. The waveform of pulse current density (J_p), and overall charge input (C), were adjusted to tune the surface morphology and optimize the electrocatalytic activity of the resultant SPCE|NiBi_(PED). Unless otherwise noted, SPCE|NiBi_(CED) and SPCE|NiBi_(CED) were prepared with charge passage of 0.54 C cm⁻² at applied direct current density and pulse current density of 100 μ A cm⁻², respectively. For comparison, NiOOH coated Ni foil (Ni|NiOOH) was prepared by using cyclic voltammetry at a scan rate of 25 mV s⁻¹ between 0.98 and 1.58 V (vs. RHE) for 100 cycles in 0.1 M NaOH.

Preparation of the *α*-**Fe**₂**O**_{3NR}|**NiBi photoanode.** The α-Fe₂O₃ nanorods (α -Fe₂O_{3NR}) photoanode was prepared by firstly depositing β-FeOOH nanorods, with ~600 nm in length and ~50 nm in diameter, onto the FTO substrate (2.0 cm²) by using CBD in a bath solution containing iron chloride hexahydrate (0.15 M) and urea (6.25wt%) at 90 °C for 4 h, followed by thermal annealing at 750 °C for 20 min. Thereafter, the *α*-Fe₂O_{3NR} photoanode was surface-modified with NiBi by PED with the passage of a charge of 0.54 C cm⁻² at a pulse current density of 100 μA cm⁻². The resultant electrode is designated as *α*-Fe₂O_{3NR}|NiBi.

Physical Characterization. The surface morphology of the deposited films was characterized using a Hitachi SU-8010 scanning electron microscope (SEM) equipped with energy-dispersive X-

ray spectroscopy (EDS). Further structure analysis of individual NiBi, scraped from the SPCE substrate, was carried out using transmission electron microscopy (TEM) and high resolution TEM (HRTEM, JEM-2100F Transmission Electron Microscope, JEOL Ltd., Japan). Raman spectra of the resultant film were collected by using a Raman spectrometer (Thermo scientific DXR Raman) with 532 nm laser and 50 µm pinhole as light filter. The amount of Ni species loaded on SPCE|NiBi was determined by using Horiba Jobin Yvon JY 2000-2 ICP optical emission spectrometer.

Electrochemical and Photoelectrochemical Characterization. Electrochemical characterizations, including cyclic voltammetry and linear sweep voltammetry, on the electrocatalytic properties of the modified electrodes were performed with a CHI 760E electrochemical workstation at room temperature. A conventional three-electrode electrochemical cell was employed with SPCE|NiBi_(CED), SPCE|NiBi_(PED), α -Fe₂O_{3NR}, or α -Fe₂O_{3NR}|NiBi_(PED) as the working electrode, Pt foil (exposed area 4.0 cm²) as counter electrode, and Hg/HgO (1.0 M NaOH) as reference electrode. Prior to each electrochemical experiments, SPCE|NiBi was pre-treated using cyclic voltammetry, at a scan rate of 10 mV s⁻¹ between 0 and 0.9 V vs. Hg/HgO (6.0 M NaOH), in 0.1 M NaOH for 10 cycles. 95% of iR drop was compensated for all the electrochemical and photoelectrochemical characterization and all potentials are reported against reversible hydrogen electrode (RHE) by using following equation (Eq. 1):

E (V vs. RHE) = E (V vs. Hg/HgO) + $0.08 + 0.059 \times pH - 0.95 \times iR_u$,

where R_u is the uncompensated resistance, measured at open circuit potential, and i is the current flowing through the cell.

Photoelectrochemical (PEC) properties of α -Fe₂O_{3NR}|NiBi_(PED) (exposed area of ~0.9 cm²) were examined in a two-compartment, separated with a Nafion[®] 117 film, three-electrode electrochemical cell using chronoamperometry at an applied potential of 1.48 V *vs*. RHE under light illumination (AM 1.5 G 100 mW cm⁻²) provided by a solar light simulator (XES-40S2-CE, SAN-EI Electric)

Formate and hydrogen measurement. The amount of formate generated from SPCE|NiBi_(CED), SPCE|NiBi_(PED), and α -Fe₂O_{3NR}|NiBi_(PED) after controlled potential electrolysis and PEC experiments was determined using an ion chromatography (883 Basic IC plus, Metrohm) equipped with Metrosep Organic Acids (7.8 * 250 mm) and Metrosep Organic Acids Guard (4.6 * 50 mm). Hydrogen generated from the Pt cathode was quantified by headspace gas analysis with an Agilent 7890A Series gas chromatography (GC) equipped with a 5 Å molecular sieve column (N₂ carrier gas at a flow rate of approximately 3 mL min⁻¹). 20 µL aliquots of the headspace gas were removed from the cathodic compartment of the PEC cell for GC analysis at the end of the experiment. The GC oven holding the columns was kept at 40 °C, and a thermal conductivity detector was used. The two-compartment electrochemical cell was purged with 2% CH₄ in N₂ (methane acts as internal standard for H₂ quantification by GC).

Table S1 Summary of amount of generated formate, formate production rate, and Faradaic efficiency from 2-h controlled-potential electrolysis at an applied potential of 1.48 V vs. RHE.

	Sample		
	SPCE NiBi _(CED)	$\text{SPCE} \text{NiBi}_{(\text{PED})}$	Ni NiOOH
Charge input (C cm ⁻²)	77.38 ± 1.09	90.00 ± 4.069	16.30 ± 1.8
Net production of formate after 2-h CPE (μmole cm ⁻²)	180.11 ± 13.15	216.23 ± 16.08	32.47 ± 3.17
Average production rate of formate (µmole cm ⁻² h ⁻¹)	90.05 ± 6.57	108.12 ± 8.04	16.24 ± 1.94
Faradaic efficiency for formate (%)	89.84 ± 6.46	92.69 ± 4.55	76.87 ± 2.60



Figure S1 Typical pulse current waveform used in this study.



Figure S2 The SEM images of (a) SPCE|NiBi_(CED) and (b) SPCE|NiBi_(PED).



Figure S3 (a-b) Raman spectra of (i) SPCE|NiBi_(CED) and (ii) SPCE|NiBi_(PED).



Figure S4 Chronopotentiograms recorded during electrodeposition of NiBi under (i) CED and (ii) PED modes in 0.1 M borate buffer (pH 9.2) containing 0.5 mM nickel sulfate.



Figure S5 Chronopotentiograms, recorded at various pulse current densities: (a) 25 μ A cm⁻², (b) 50 μ A cm⁻², (c) 200 μ A cm⁻², and (d) 400 μ A cm⁻², during electrodeposition of NiBi_(PED) in 0.1 M borate buffer (pH 9.2) containing 0.5 mM nickel sulfate. Total charge passage for all the deposition: 0.54 C cm⁻².



Figure S6 SEM images of SPCE|NiBi_(PED) prepared at various pulse current densities, ranging from (a, a') 25 μ A cm⁻², (b, b') 50 μ A cm⁻², (c, c') 200 μ A cm⁻², and (d, d') 400 μ A cm⁻². Total charge passage for all the samples: 0.54 C cm⁻². Scale bar: 500 nm.



Figure S7 Laviron plots of (a) SPCE $|NiBi_{(CED)}$ and (b) SPCE $|NiBi_{(PED)}$ in 0.1 M NaOH.



Figure S8 (a-b) Chronoamperograms of SPCE|NiBi_(CED) (a) and SPCE|NiBi_(PED) (b) recorded at an applied potential of 1.48 V vs. RHE in 0.1 M NaOH containing methanol of various concentration ranging from (i) 0, (ii) 5, (iii) 10, (iv) 15, (v) 20, (vi) 25, (vii) 50, (viii) 75, to (ix) 100 mM. (c-d) Plots of J_{cat}/J_L vs. $t^{1/2}$ for SPCE|NiBi_(CED) (c) and SPCE|NiBi_(PED) (d) using the curves obtained with (i) 5, (ii) 10, (iii) 15, (iv) 20, and (v) 25 mM methanol in (a) and (b).



Figure S9 Chronoamperogram of SPCE|NiBi_(PED) recorded at an applied potential of 1.78 V vs. RHE in 0.1 M NaOH containing 0.1 M methanol. The significant fluctuations in current density was resulted from vigorous OER.



Figure S10 (a) Top-view and (b) cross-sectional view of SEM images of α -Fe₂O_{3NR}. Scale bar: 1 μ m.



Figure S11 Chronoamperogram of the pristine α -Fe₂O_{3NR} photoanode recorded at an applied potential of 1.48 V vs. RHE in 0.1 M NaOH containing 0.1 M methanol under light illumination.