Electronic Supplementary Information

for

Facile growth of transition metal hydroxide nanosheets on porous nickel foam for efficient electrooxidation of benzyl alcohol

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Experimental

1. Preparation of transition metal hydroxide nanosheets on Ni foam

Transition metal hydroxide ($M(OH)_2$, M = Ni or Co) nanosheets were grown on porous nickel foam by a facile electrodeposition method[1-3]: A piece of nickel foam (1.5 mm, 380 g/m^2) with a surface area of 1×1 cm^{-2} was immersed in a 0.1 M $Ni(NO_3)_2$ (or $Co(NO_3)_2$, Aladdin Co.) aqueous solution, while the rest of the electrode was sealed with epoxy resin adhesive. Electrodeposition was performed at a constant current mode (cathodic current, 10 mA) for 5 min by using a CHI840D electrochemical workstation (CH Instruments, Inc.). Platinum mesh (1×1 cm^2) and saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The as-deposited samples were then dried in air, and were denoted as Ni-OH/NF and Co-OH/NF. Prior to the experiments, Nickel foam (3 cm $\times$ 1 cm) was carefully cleaned with 1 M HCl aqueous solution (Sinopharm Chemical Reagent Co. (SCRC)) in an ultrasound bath for 10 min in order to remove the surface NiO layer, and then deionized water and absolute ethanol were used for 3 min each to ensure the surface of the Ni foam was well cleaned. The cleaned nickel foam was dried in vacuum (60 ^{o}C, 1h).

2. Characterization

XRD patterns were collected on a Miniflex 600 X-ray diffractometer (Rigaku Co.) with Cu Kα radiation. SEM images and EDS mappings were obtained on a ZEISS SIGMA 300 field emission scanning electron microscope at an accelerating voltage of 5 kV. TEM image was measured on a FEI Tencai 20 transmission electron microscope at an accelerating voltage of 200 kV. Sample for TEM was prepared by ultrasounding in ethanol. XPS measurements were carried out by using a VG Scientific ESCA Lab Mark II spectrometer equipped with an Mg X-ray source. The binding energy calibration of the spectra has been

referred to C 1s peak located at 284.4 eV for the analysis. Electrochemical studies were performed using a CHI760E electrochemical workstation (CH Instruments, Inc.). Platinum mesh (1×1 cm^2) and saturated Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The Ag/AgCl electrode was caliberated with respect to RHE. The calibration was performed by a reported method.[4] In 1 M NaOH aqueous solution, E (RHE) = E (Ag/AgCl) + 0.98 V (see Figure S9). Further, before LSV tests, the iR drop was automatically corrected on the electrochemical workstation. The iR compensation test was conducted at a compensation level of 95%, and the iR compensation modes was set to automatic. For LSV, the scan rate was set at 1 mV s^{-1}.

3. Electrooxidation of BnOH

The catalytic activities of the as-prepared porous electrodes for the electrooxidation of BnOH (0.1 M) were investigated in 1 M NaOH aqueous solution in a constant current model with different current densities. For three-electrode configuration, the as-prepared porous electrode, platinum mesh (1×1 cm^2) and saturated Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. For two-electrode configuration, the as-prepared porous electrode and platinum mesh (or Ni foam, 1×1 cm^2) were used as the anode and cathode, respectively. Evolving H$_2$ gas was measured *via* directly injecting 200 μL of the gas from the headspace of the electrolytic cell into a Shimazu GC2014C gas chromatograph (TCD, molecular sieve 5A column, Ar carrier) by bubbling with argon (30 mL/min). The products of the oxidation of BnOH were analyzed by GC technique (6820, Agilent Co., FID, HP-5 capillary column, N$_2$ carrier). Prior to GC analysis, 4 mL of the reaction solution was acidized by 0.8 mL of HCl aqueous solution (36 *wt*.%, SCRC), and then 4 mL of dichloromethane (SCRC) was added into the reaction solution. After stirring

for 3 min and standing for 1 min, the organic phase was moved to a sample vial (10 mL), and was dehydrated by adding a certain amount of Na_2SO_4 (SCRC). Then, 2 μL of the sample was injected for GC analysis. Benzoic acid (BnCOOH) and benzaldehyde (BnCHO) are detected as the products for the electrocatalytic oxidation of BnOH.

The Faradic efficiency (FE) was calculated by using the following equation for the electrooxidation of BnOH:

$$FE\ (\%) = \frac{2F(mol\ of\ BnCHO) + 4F(mol\ of\ BnCOOH)}{Total\ passed\ charge} * 100$$

Where F is the Faraday constant (96,485 C mol^{-1}).

To obtain pure BnCOOH, 12 mL HCl aqueous solution (36 *wt.*%, SCRC) was added into the electrolyte after the electrooxidation reaction. Then, BnCOOH containing NaCl was separated from the electrolyte by centrifuging. The obtained sample was washed with 3 M HCl aqueous solution and dried in vacuum at 60 °C.

References

1. M.T. Bender, Y.C. Lam, S. Hammes-Schiffer and K. Choi, *J. Am. Chem. Soc.*, 2020, **142**, 21538.

2. A. Roy, H.S. Jadhav, G.M. Thorat and J. G. Seo, *New J. Chem.*, 2017, **41**, 9546.

3. X. Yang, A. Lu, Y. Zhu, M.N. Hedhili, S. Min, K. Huang, Y. Han and L. Li, *Nano Energy*, 2015, **15**, 634.

4. Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nature Mater.*, 2011, **10**, 780.

Figure S1. (a) Particle size distribution and (b) high-resolution SEM image for sample Ni-OH/NF.
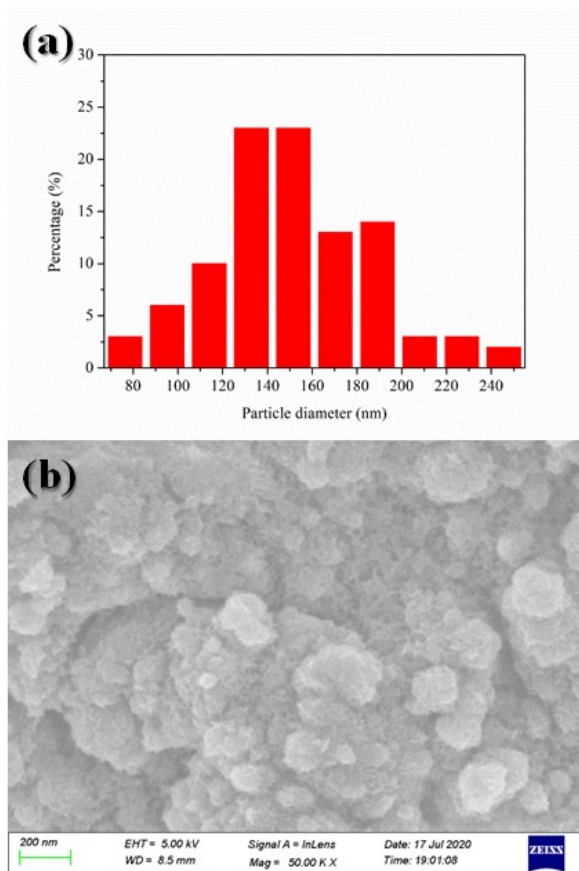
Figure S2. LSV curves of different electrodes in 1 M NaOH aqueous solution with 0.1 M

BnOH in a three-electrode configuration.
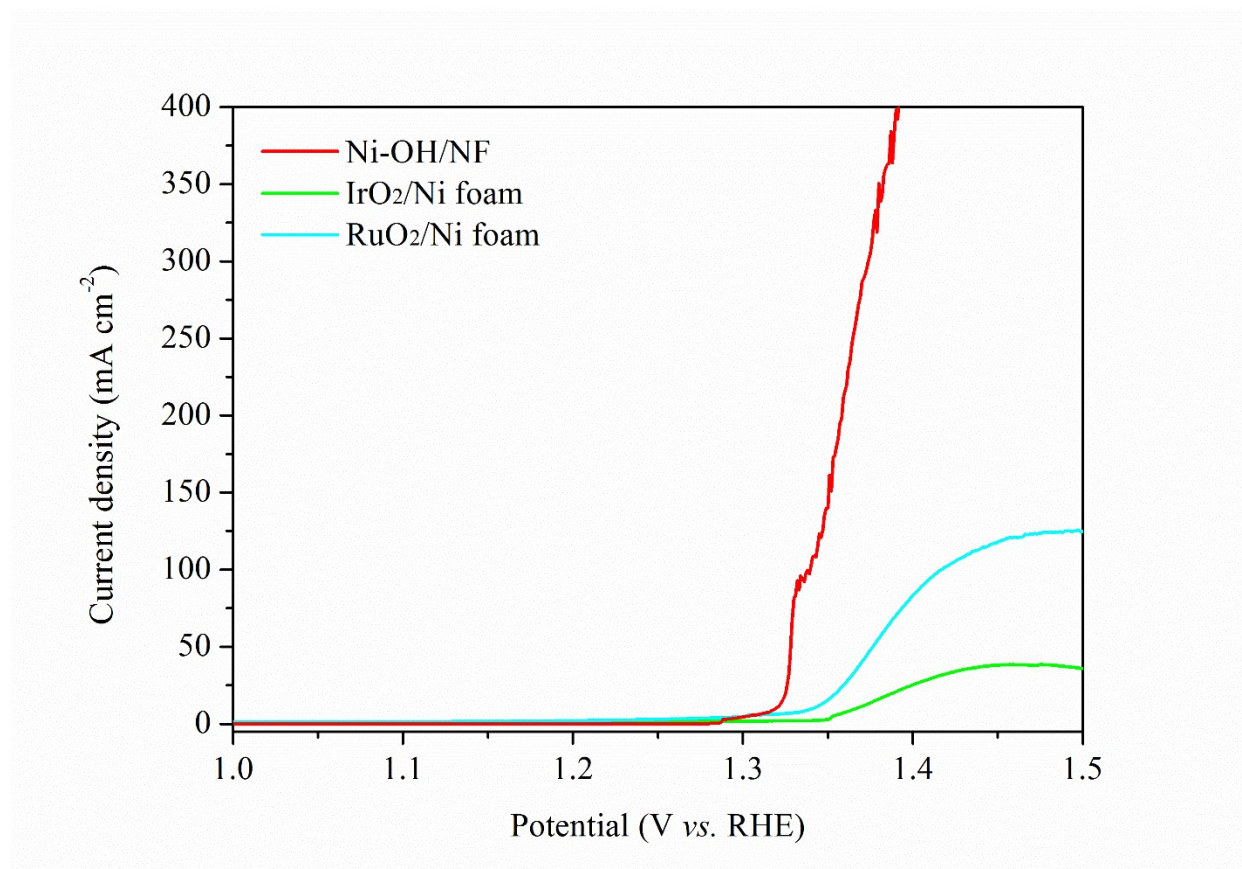
Note: RuO$_2$/Ni foam (or IrO$_2$/Ni foam) electrode was prepared by loading RuO$_2$ (or IrO$_2$,

Adamas Reagent Co.) on Ni foam with a loading amount of 2.5 mg cm^{-2}, in which a polymer

binder (Nafion, Alfa Aesar Co.) was introduced for a purpose of fixation.

Figure S3. XRD patterns for sample Ni-OH/NF before and after multiple electrooxidation cycles.
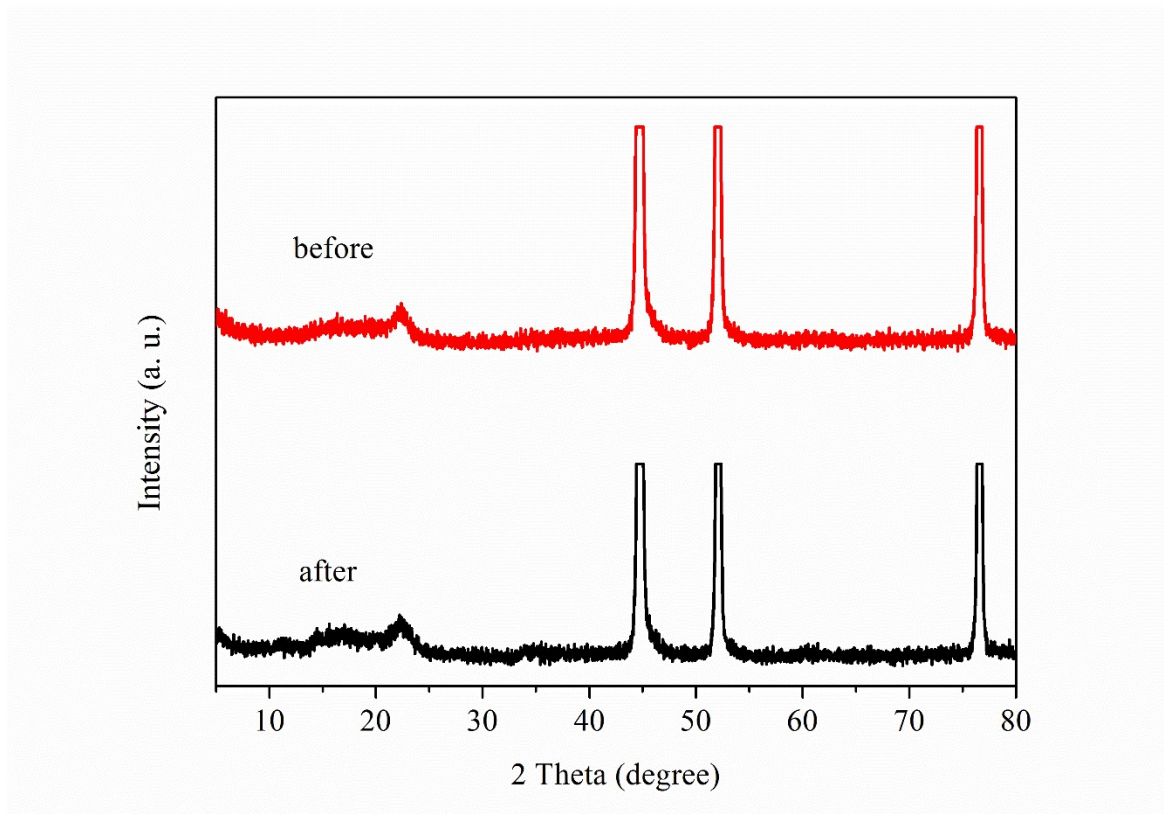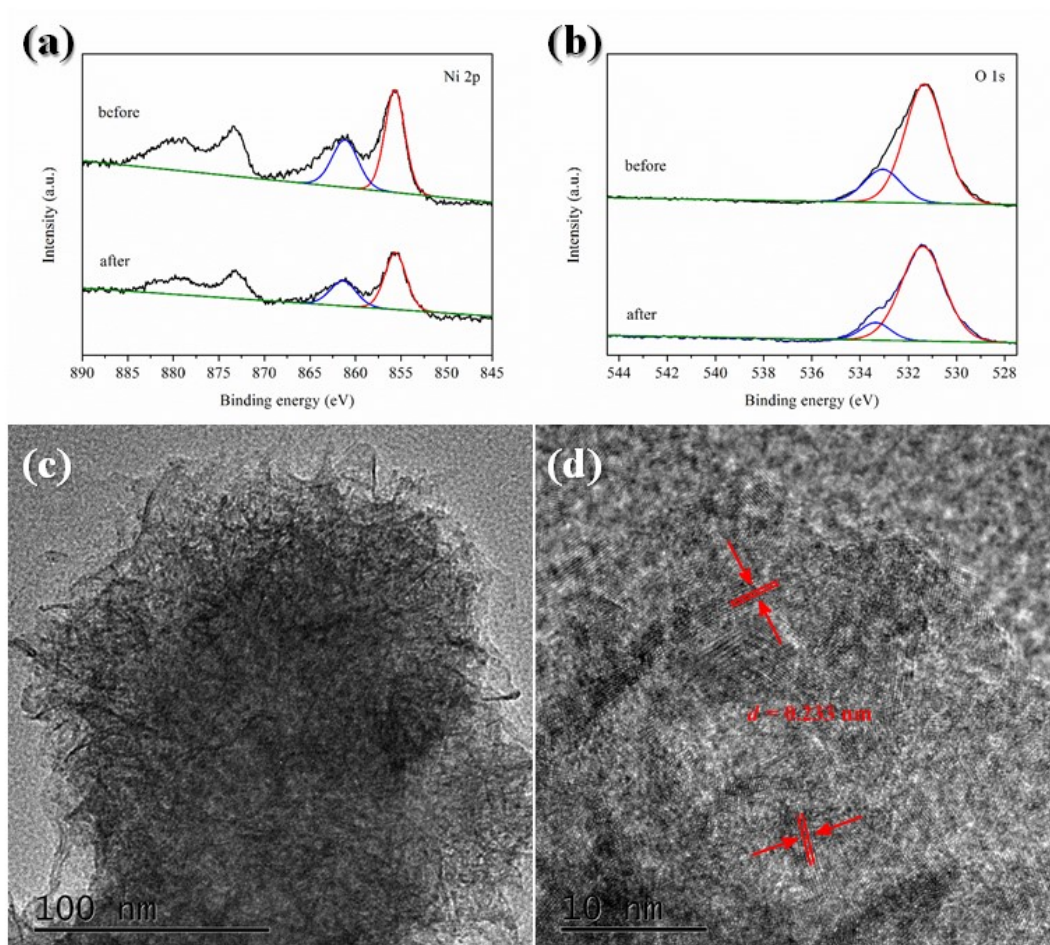
Figure S4. EDS mappings for sample Ni-OH/NF (a-c) before and (d-f) after multiple electrooxidation cycles.
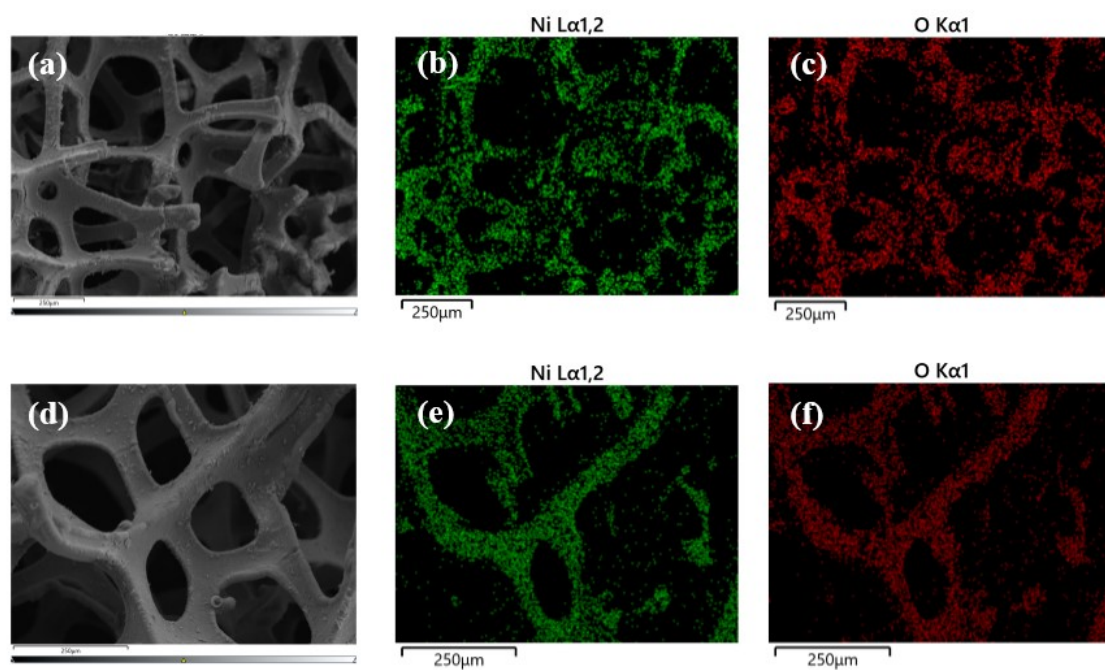
Figure S5. High-resolution XPS spectra of (a) Ni 2p and (b) O 1s, and (c, d) TEM images for sample Ni-OH/NF after multiple electrooxidation cycles.

Figure S6. (a) Electrolytic voltages at different current densities for the reported hybrid water electrolysis system and (b) the conversion of BnOH, the selectivity of BnCOOH and the Faradic efficiency for the electrooxidation of BnOH at 50 mA cm^{-2} for various samples in a two-electrode configuration.
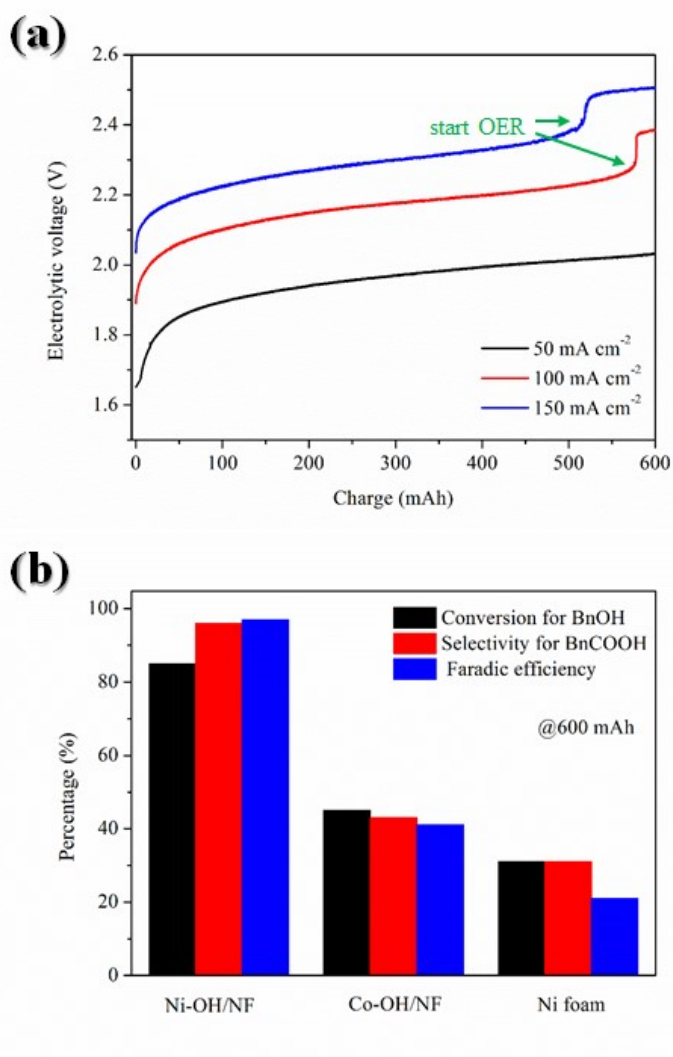
Figure S7. (a) Photograph and (b) XRD pattern for the obtained BnCOOH.
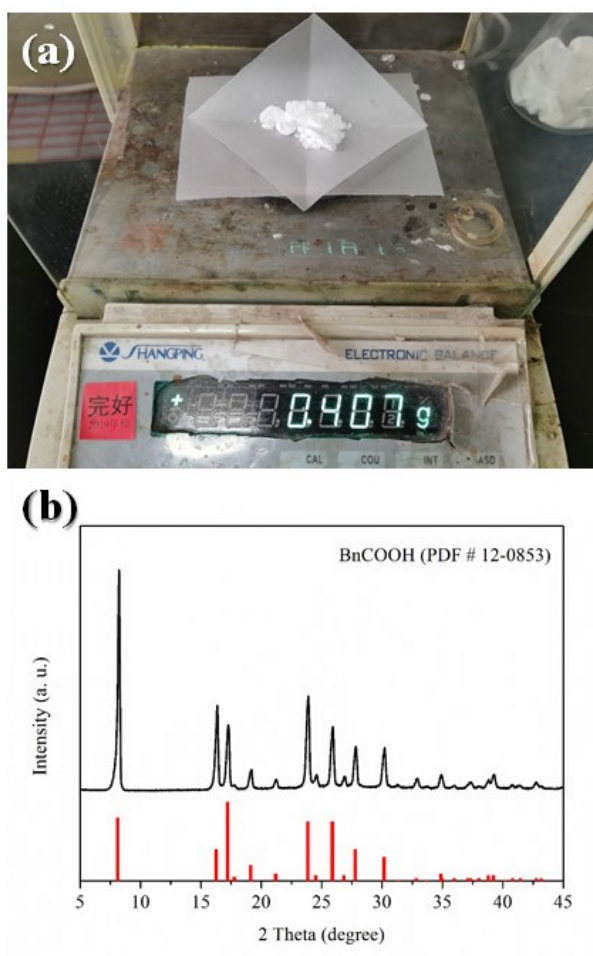
Figure S8. *J-V* characteristics of the photovoltaic cell under simulate solar light. The inset is the photograph for the photovoltaic cell.
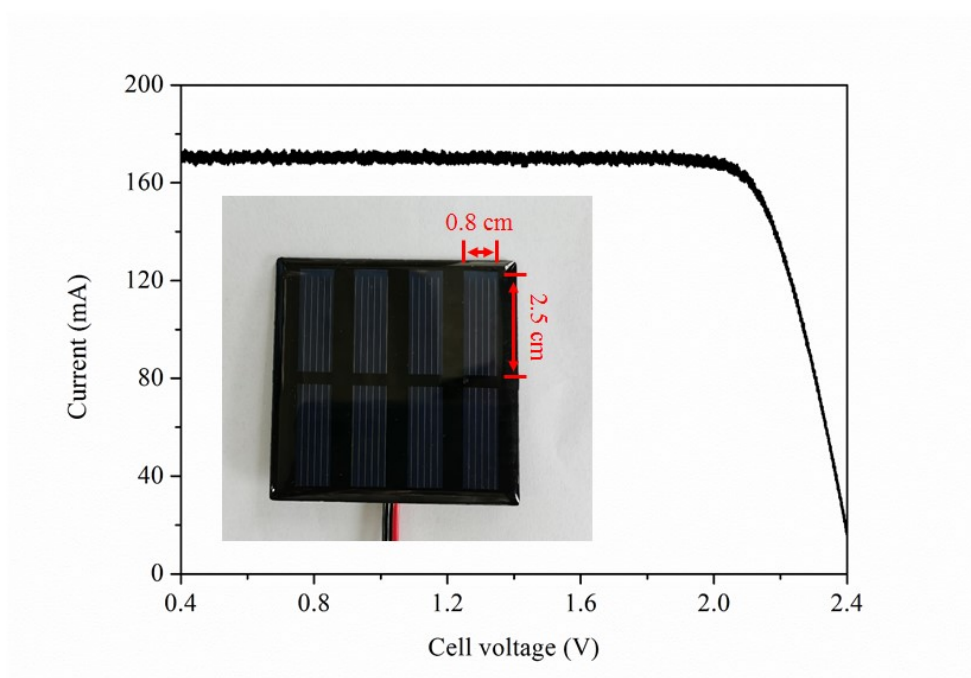
Figure S9. Cyclic voltammetry curve of Pt sheet in 1 M NaOH aqueous solution under H_2 atmosphere.