

**Supporting Information for**

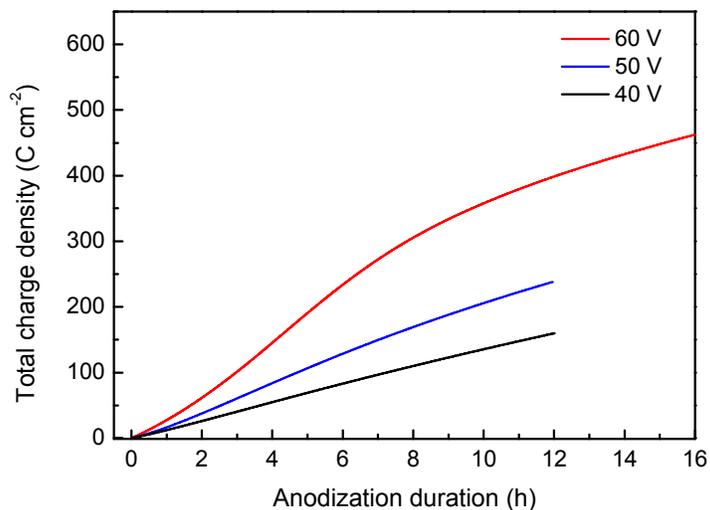
# Efficient Photoelectrochemical Water Splitting over Anodized *p*-Type NiO Porous Films

*Chenyan Hu, Kenneth Chu, Yihua Zhao, Wey Yang Teoh\**

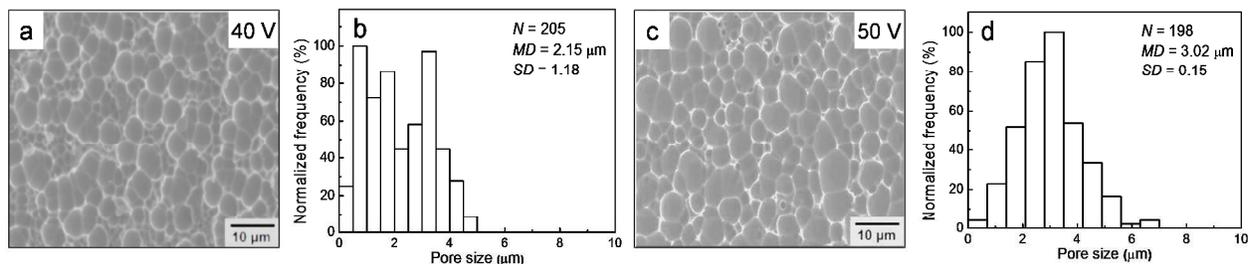
Clean Energy and Nanotechnology (CLEAN) Laboratory, School of Energy and Environment,  
City University of Hong Kong, Kowloon, Hong Kong S.A.R.

\*Corresponding E-mail: [wyteoh@cityu.edu.hk](mailto:wyteoh@cityu.edu.hk)

## 1. Anodization synthesis parameters and the influence on NiO morphologies



**Figure S1.** Total charge density for the anodization of Ni foil under different applied voltages. Electrolyte: 0.5 wt.% KOH, 5 wt.% Milli-Q water and 94.5 wt.% glycerol; Counter electrode: Pt ring.

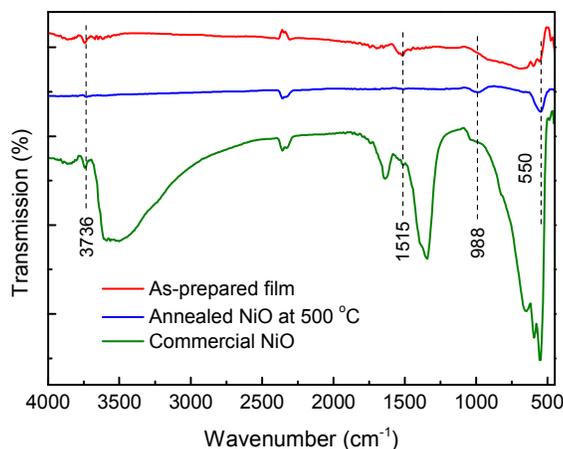


**Figure S2.** Plan-view images of Ni foils anodized at voltage of (a) 40 V and (c) 50 V for 12 h and the respective pore size distributions (b) and (d), also showing the mean diameter (*MD*) and standard deviation (*SD*) calculated from sample size (*N*).

**Table S1.** The arithmetic and geometric pore sizes of NiO electrodes anodized under different durations and voltages.

Anodization duration (h)	Anodization voltage (V)	Arithmetic mean diameter ( $\mu\text{m}$ )	Arithmetic standard deviation	Geometric mean diameter ( $\mu\text{m}$ )	Geometric standard deviation
0.5	60	0.23	0.11	0.19	1.90
2	60	0.47	0.30	0.30	3.44
4	60	0.70	0.21	0.66	1.41
8	60	3.00	1.12	2.82	1.48
12	60	3.25	0.98	2.99	1.42
24	60	3.91	1.42	3.59	1.49
12	40	2.15	1.18	1.75	2.03
12	50	3.02	0.15	2.81	1.45

## 2. Fourier transform infrared spectroscopy (FTIR) analyses



**Figure S3.** FTIR spectra of as-anodized film (60 V, 12 h) and that after annealing (500 °C, 6 h). Also shown is the spectrum for commercial NiO nanoparticles (Aldrich). The peak at 3736  $\text{cm}^{-1}$  is assigned to the stretching vibration of non-hydrogen-bonded, free hydroxyl groups (OH) from the  $\text{Ni}(\text{OH})_2$ , while that at 550  $\text{cm}^{-1}$  is ascribed to the stretching vibration of NiO. The peak at 1515  $\text{cm}^{-1}$  in the as-anodized film is currently unidentified.

### 3. Adsorption isotherm of methyl orange on commercial NiO nanoparticles.

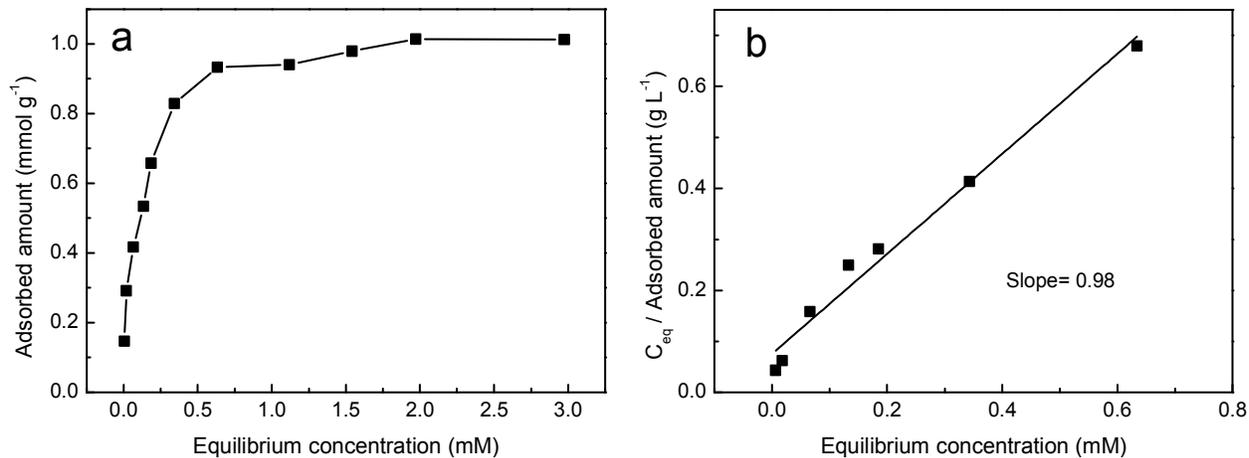
The area of NiO occupied by each methyl orange (MO) molecule was estimated according to work of Bandara *et al.*<sup>1</sup> Eleven aqueous solutions at pH 3.5 containing 2 g L<sup>-1</sup> NiO particles were prepared with MO concentrations ranging from 0.3 to 5 mM. The amber vials containing the NiO particles and dye solutions were capped tightly and stirred for 24 h at room temperature. The concentration of MO in the supernatant was determined by its optical density at 463 nm (Varian, Cary 50). The obtained adsorption isotherm plot of MO at pH 3.5 for NiO is shown below in Figure S4a. The adsorption of MO on NiO can be adequately described by the Langmuir isotherm:

$$q = q_m \frac{K C_{eq}}{1 + K C_{eq}} \quad (1)$$

Or

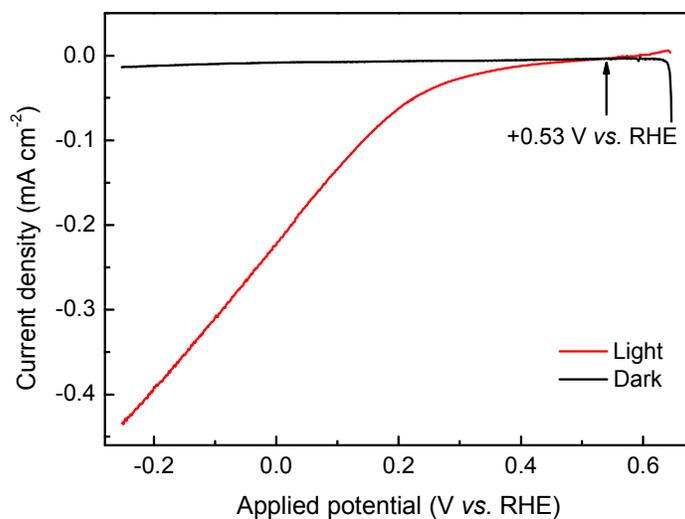
$$\frac{C_{eq}}{q} = \frac{1}{Kq_m} + \frac{C_{eq}}{q_m} \quad (2)$$

where  $q$  (mmol g<sup>-1</sup>) is the adsorbed amount of MO on NiO at different equilibrium concentrations,  $q_m$  (mmol g<sup>-1</sup>) is the maximum amount of MO forming the monolayer on NiO,  $K$  is the equilibrium constant and  $C_{eq}$  is the equilibrium concentration (mM). The plot of  $C_{eq}/q$  versus  $C_{eq}$  (from 0 to 0.7 mM) is linear with a slope of  $1/q_m$ , which is shown in Figure S4b, so the calculated  $q_m$  is 1.02 mmol g<sup>-1</sup>. The specific surface area of the commercial NiO particles, determined from N<sub>2</sub> adsorption (BET) measurement, is 112 m<sup>2</sup> g<sup>-1</sup>, so the area of NiO occupied by each MO molecule is 0.18 nm<sup>2</sup>.



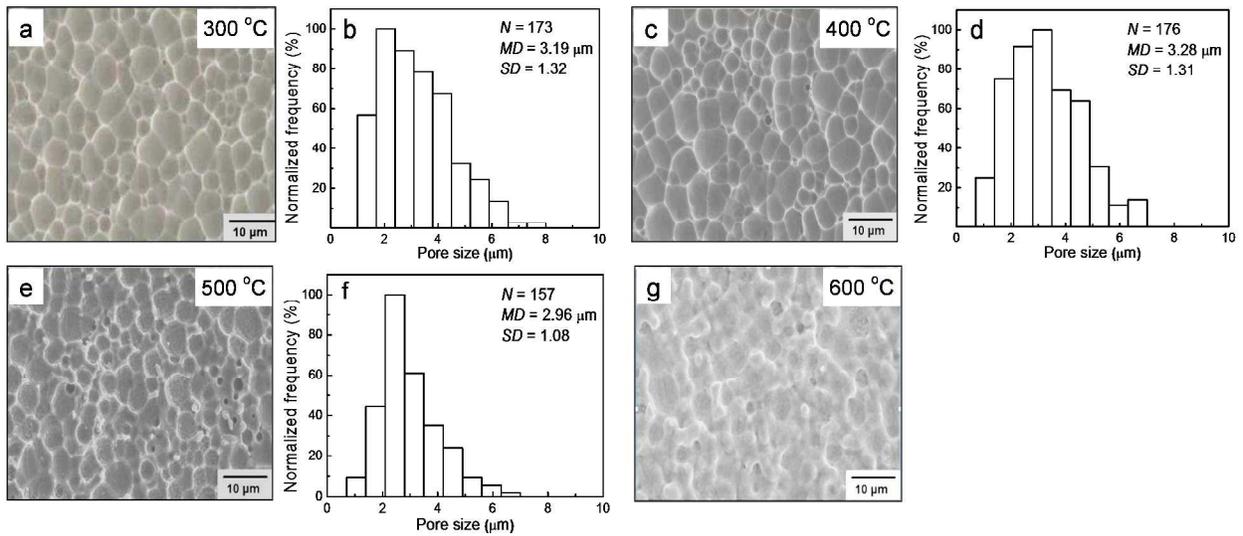
**Figure S4.** (a) Adsorption isotherm of MO at pH 3.5 on NiO. (b) The plot of  $C_{eq}/q$  versus  $C_{eq}$  in low concentration range.

#### 4. Determination of the onset potential



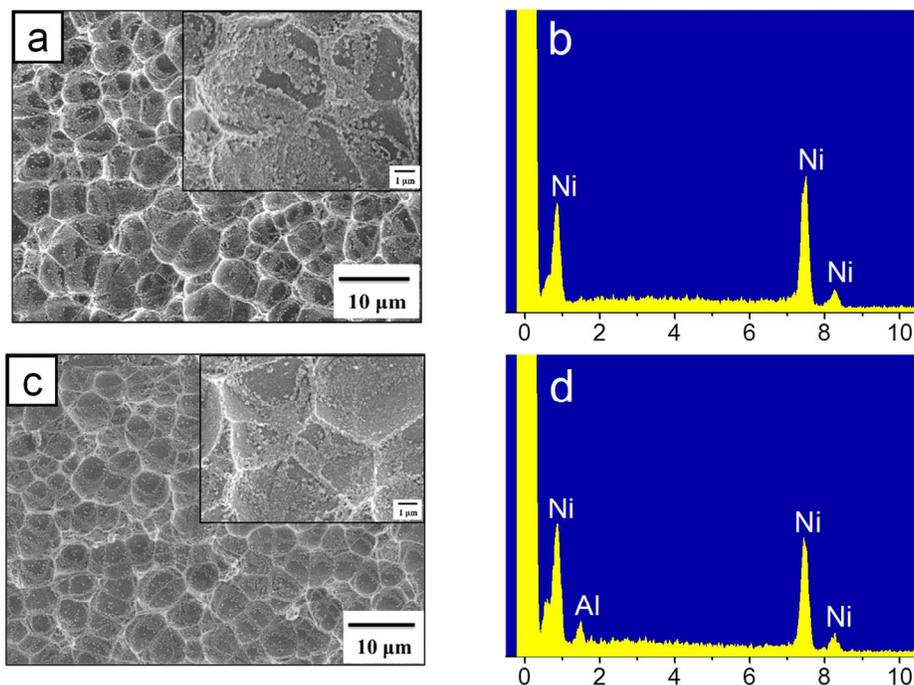
**Figure S5.** Linear sweep voltammetry of NiO photoelectrode measured in 0.1 M NaClO<sub>4</sub> electrolyte under dark and light conditions. The representative sample shown here was prepared via anodization at 60 V for 12 h and annealed at 500 °C for 6 h. Similar onset potentials were also measured for other samples.

## 5. Effect of annealing temperatures on NiO morphology



**Figure S6.** Plan-view images of anodized Ni foils (60 V, 12 h) annealed at temperature of (a) 300, (c) 400, (e) 500 and (g) 600 °C, and the corresponding pore size distributions (b), (d) and (f) showing the mean diameter ( $MD$ ) and standard deviation ( $SD$ ) calculated from sample size ( $N$ ). Note the small influence of annealing temperatures on the NiO pore size distribution at 500 °C and below. At 600 °C, sintering of pores took place, which distributions could not be easily measured.

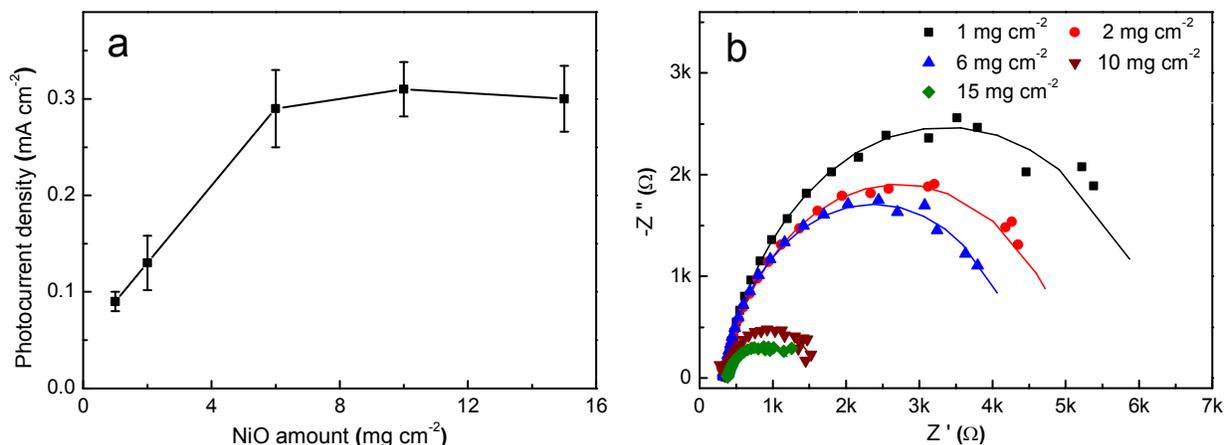
## 6. Morphology of NiO electrode before and after coating with Al<sub>2</sub>O<sub>3</sub> layer



**Figure S7.** FE-SEM images and energy dispersive X-ray (EDX) analyses of (a, b) bare NiO and (c, d) Al<sub>2</sub>O<sub>3</sub>/NiO electrodes. The inset of (a) and (c) are the magnified images of bare NiO and Al<sub>2</sub>O<sub>3</sub>/NiO electrodes, respectively.

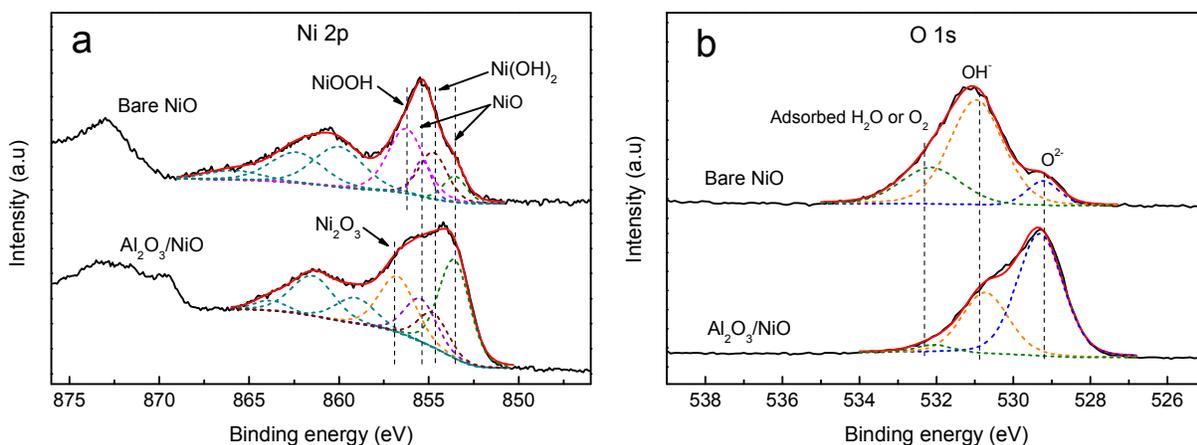
## 7. Optimization of photoelectrode fabricated from commercial NiO source

Suspension containing 2 mg L<sup>-1</sup> of commercial NiO nanoparticles (99.8%, Aldrich) in absolute ethanol (>99.5%, Aldrich) was sonicated for 1 h and dropcast onto cleaned fluorine-doped tin oxide glass (FTO, Nippon Special Glass, 7 Ω/□) within an area of 5 cm<sup>2</sup>. Dropcast was carried out stepwise with 0.5 mL suspension each time. The dropcast substrate was calcined at 400 °C (ramping 5 °C min<sup>-1</sup>) for 1 h in a muffle furnace. Figure S8a shows the optimization of NiO loading, showing optimum photocurrent at 6 mg L<sup>-1</sup> and charge transfer resistance (Figure S8b).



**Figure S8.** (a) Photocurrent density and (b) Nyquist plots of commercial NiO electrodes measured at  $-0.25$  V vs. RHE under full arc irradiation as a function of the particles loading on FTO.

### 8. XPS spectra of bare NiO and Al<sub>2</sub>O<sub>3</sub>/NiO electrodes after water splitting



**Figure S9.** (a) Ni 2p and (b) O 1s spectra of bare NiO and Al<sub>2</sub>O<sub>3</sub>/NiO electrodes after photoelectrochemical water splitting for 20 h. Black solid lines show the experimental measured spectra, while the red solid lines show the net sum of the deconvoluted peaks of various components (broken lines).

## 9. Determination of turnover frequency (TOF)

Turnover frequencies (TOFs) were calculated by taking into account all NiO molecules on the electrode surface and the rate of H<sub>2</sub> molecules evolved, assuming Faradaic efficiency of 100% - A verified assumption as shown in Table 2 in the main text.  $TOF = I_{pc} \text{ (A m}^{-2}\text{)} \times a^2 \text{ (m}^2\text{)} \times 6.241 \times 10^{18} \text{ (s}^{-1} \text{ A}^{-1}\text{)} / (n \times N \times RF)$ , where  $I_{pc}$  is the photocurrent density of NiO electrode,  $a$  is the unit cell edge length of the cubic NiO ( $4.1771 \times 10^{-10}$  m),  $n$  is the number of electrons required for each H<sub>2</sub> evolution,  $N$  is the averaged NiO molecule number in one surface NiO cell (2 per NiO surface cell),  $RF$  is the roughness factor of the NiO electrode ( $\text{m}^2_{\text{NiO}}$  per  $\text{m}^2_{\text{electrode}}$ ). The conservative estimation assumes NiO (100) surface, which is the densest packing.

## REFERENCE

(1) Bandara, J.; Mielczarski, J. A.; Kiwi, J.; Molecular Mechanism of Surface Recognition. Azo Dyes Degradation on Fe, Ti, and Al Oxides through Metal Sulfonate Complexes. *Langmuir* **1999**, *15*, 7670-7679.