

Supplementary Materials

Base-Acid Hybrid Water Electrolysis

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Experimental section

Materials: CoO nanowires were synthesized according to previous report. In a typical procedure, 0.29 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.24 g of urea were dissolved in 15 mL of H_2O and 15 mL of ethanol to form a pink solution. The mixed solution was then placed in a 100-mL Teflon lined stainless steel autoclave. The autoclave was sealed and heated at 90°C for 8 hours and allowed to cool to room temperature. The obtained precipitates were filtered, washed with deionized water for several times, and then annealed at 250°C for 2h in N_2 flow. Then, soaking the as-prepared powder in 1 M NaBH_4 for solution for 1 h, then collected by centrifugation, washed with deionized water and dried in a vacuum oven at 80°C for 12 h. The ceramic LATSP film ($2.5 \times 2.5 \text{ cm}^2$, 150 μm in thickness) was purchased from Ohara Inc., Japan. Commercialized Pt-foil electrodes were used as received.

Electrochemical Measurements: OER catalytic electrode was prepared by mixing 80 wt % CoO nanowires, 10 wt % conductive agent (acetylene black) and 10 wt % poly (tetrafluoroethylene) (PTFE) binder in an isopropanol solution to form a homogeneous slurry, which was then rolled into a film. The film was cut into a square area of $0.4 \text{ cm} \times 0.4 \text{ cm}$ (0.16 cm^2), and then pressed onto a stainless steel mesh that was employed as current collector to form the OER catalytic electrode. Commercialized platinum-foil

electrode was used as the HER catalytic electrode directly. The onset potential of OER on CoO-nanowire-based electrode in 1 M KOH and the onset potential of HER on Pt-foil electrode in 0.5 M H₂SO₄ was investigated by linear sweep voltammetric measurements with a typical three-electrode method, in which a Pt plate and saturated calomel electrode (SCE, 0.242 V vs. standard hydrogen electrode) were used as the counter and reference electrodes, respectively. The base-acid hybrid electrolytic cell was fabricated by using CoO-nanowire-based electrode and Pt-foil electrode as OER and HER catalytic electrodes, respectively (see **Fig. 4**). A basic solution (1M KOH + 0.5M Li₂SO₄) and an acidic solution (0.5M H₂SO₄) were anodic electrolyte and cathodic electrolyte, respectively. The anodic electrolyte and cathodic electrolyte were separated by a ceramic LATSP film. Electrochemical performance of the base-acid hybrid electrolytic cell was probed by two-electrode method [CoO-nanowire-based electrode was used as work electrode; Pt-foil electrode was used as counter/reference electrode]. All of electrochemical measurements were performed with a CHI 660D electrochemistry workstation.

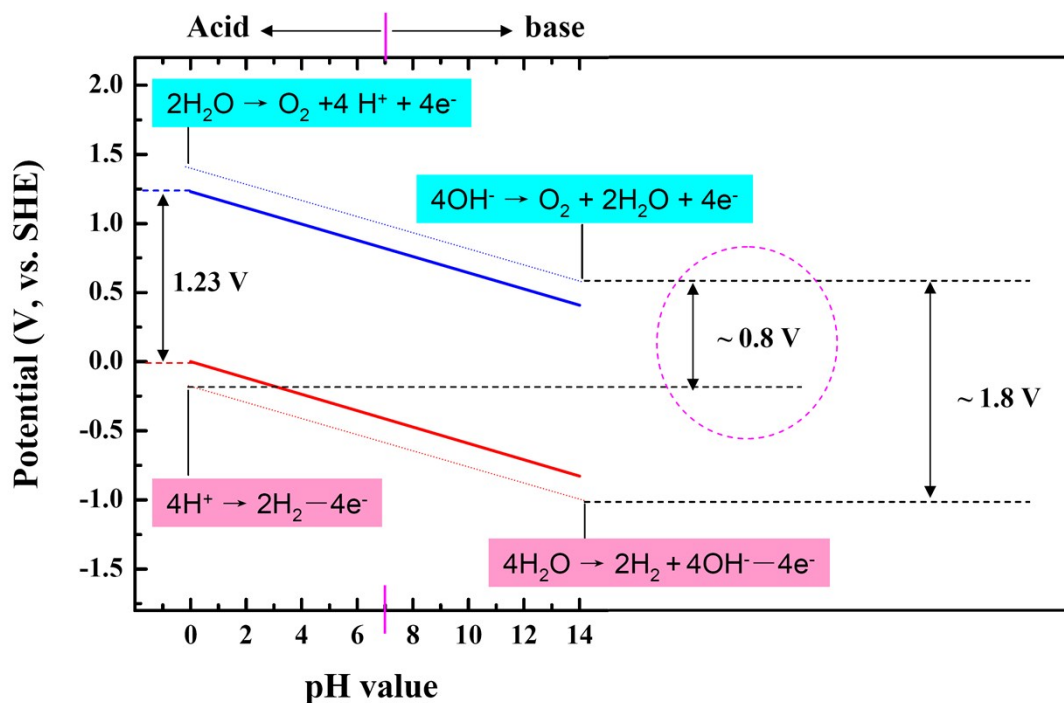


Figure S1. Potentials of oxygen-evolving reaction (OER) and hydrogen-evolving reaction (HER) in aqueous electrolyte solutions with different pH values. Red-real-line: theoretical potential for HER; Blue-real-line: theoretical potential for OER; Red-broken-line: potential for HER (theoretical potential + over potential); Blue-broken-line: potential for OER (theoretical potential + over potential).

As shown in **Fig. S1**, water electrolysis requires an applied voltage of at least 1.23 V to provide the thermodynamic driving force. Owing to the practical overpotentials associated with the reaction kinetics, however, a substantially larger voltage (1.8 ~ 2.0 V) is inevitably needed. If we combine the HER in an acid (i. e. $4\text{H}^+ \rightarrow 2\text{H}_2 - 4\text{e}^-$) and the OER in a base (i. e. $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$), a low driving voltage (~ 0.8 V) for water electrolysis would be achieved (see **Fig. S1**). It should be key reason for us to develop the base-acid hybrid water electrolysis.

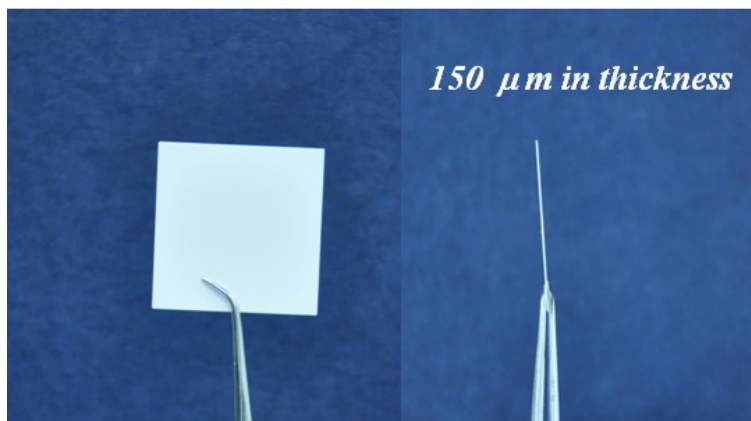


Figure S2. Photograph of LATSP ceramic film. The water-stable lithium super-ionic conductor ceramic film (LATSP, $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$) with thickness of 0.15 millimeter is the product of Ohara Inc., Japan. Its conductivity is $10^{-4} \text{ S cm}^{-1}$. LATSP is a kind of ceramic solid electrolyte for lithium-ion batteries, and has been widely investigated on the study about all solid state lithium-ion batteries¹⁻³.

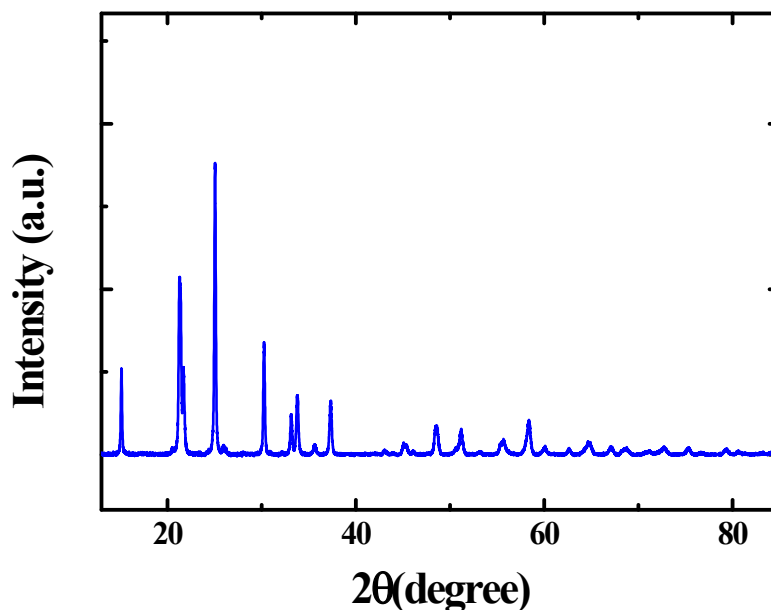


Figure S3. XRD pattern of LATSP ceramic film. As shown in **Fig. S3**, LATSP has a typical NASICON structure. The NASICON structure consists of PO_4 -tetrahedra and MO_6 -octahedra ($\text{M}=\text{Ti}$) linked by shared oxygen atoms⁴⁻⁷. There are two types of position of Li-ion localization that can be distinguished: M1 positions, surrounded by six oxygen atoms; and M2 positions, surrounded by eight oxygen atoms. Hence, a system of three dimensional channels arises, where Li-ion transport realized by alternating of positions M1 and M2^{4,5}. Accordingly, the ceramic LATSP film can permit the pass of Li-ion with high diffusion rate.

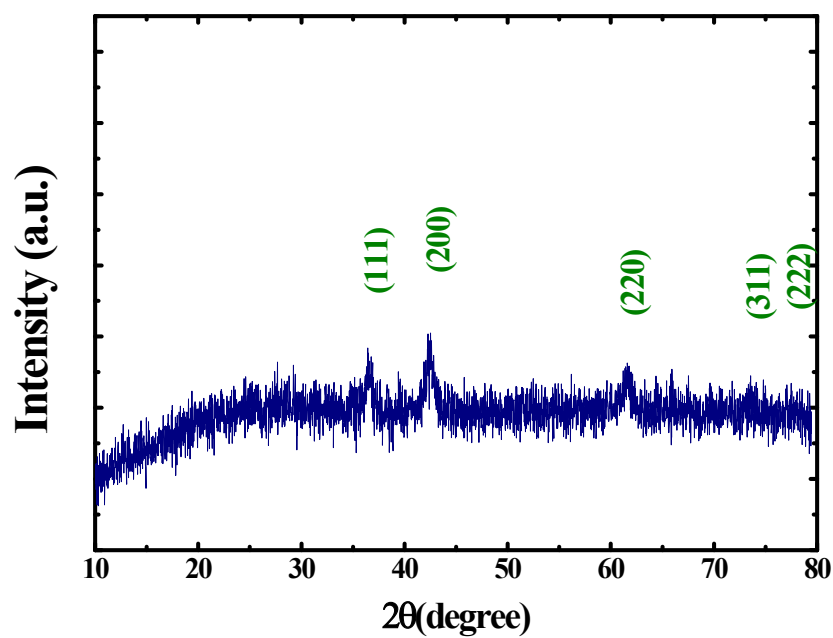


Figure S4. X-ray diffraction (XRD) pattern of CoO nanowires. The diffraction peaks in the spectrum corresponding with (111), (200), (220), (311), and (222) crystal facets from cubic CoO suggest that it has a good crystalline structure.

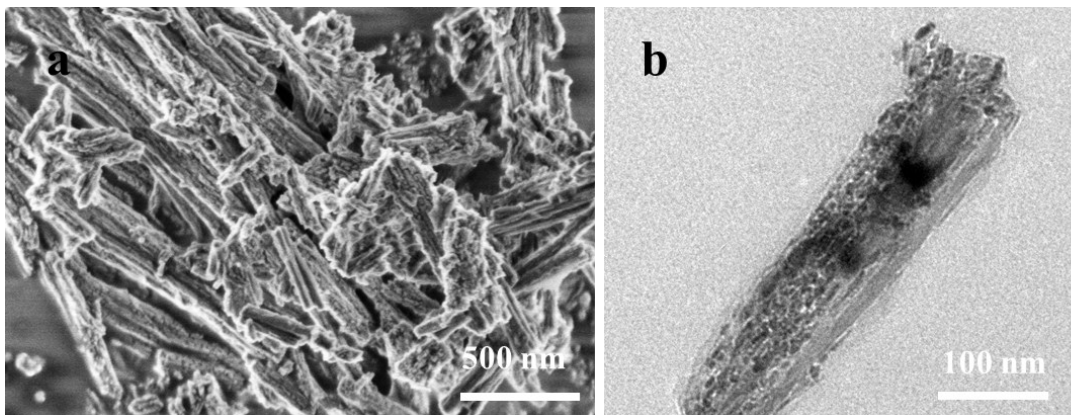


Figure S5. SEM image (a) and TEM image (b) of CoO nanowires. SEM image shows that the CoO nanowires have a uniform size with diameter of about 100 nm. TEM image suggests that each nanowire is composed of a lot of small nanoparticles with multiple mesopores.

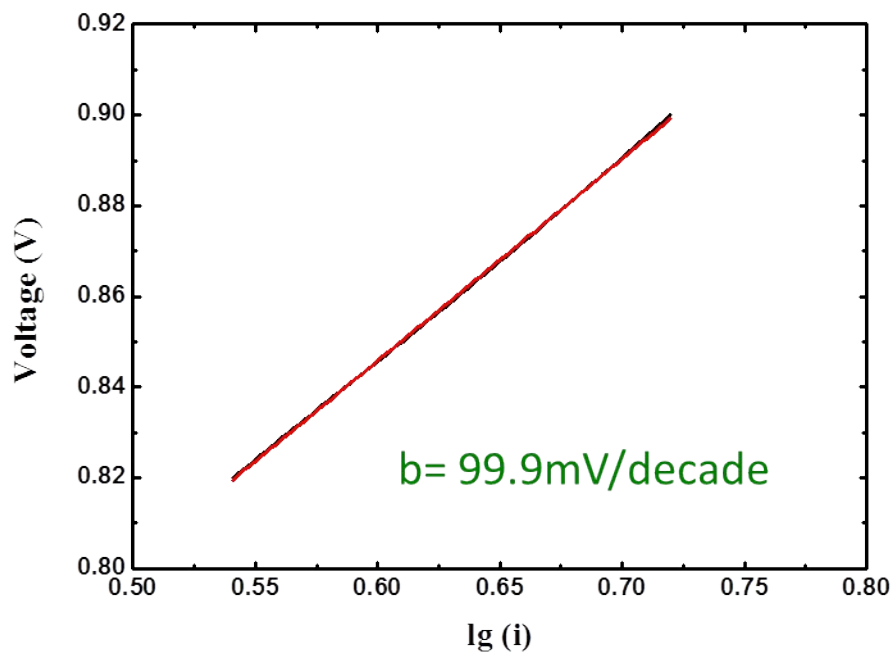


Figure S6. Tafel plots of the base-acid hybrid electrolytic cell. As shown in Figure S6, this hybrid electrolytic system yields a Tafel slope of 99.9 mV/decade, indicating that the reaction rate is low.

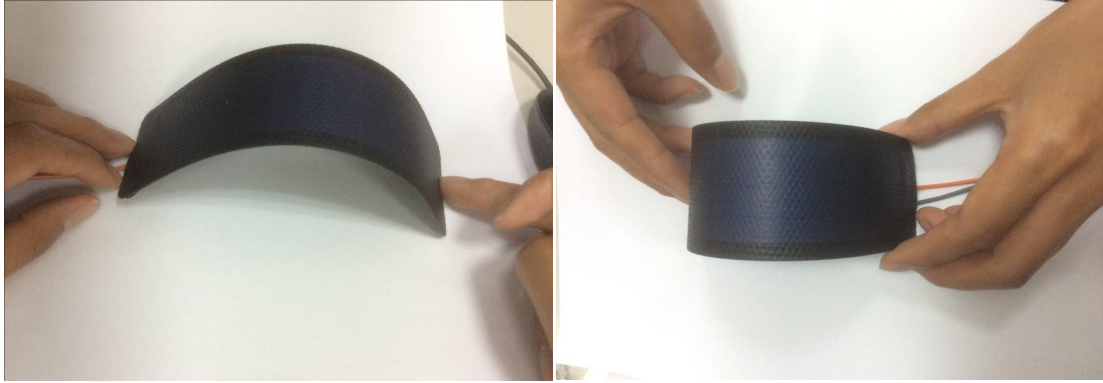


Figure S7. Photograph of the flexible solar cell purchased from Wuxi warmspace Tec. co, Ltd.

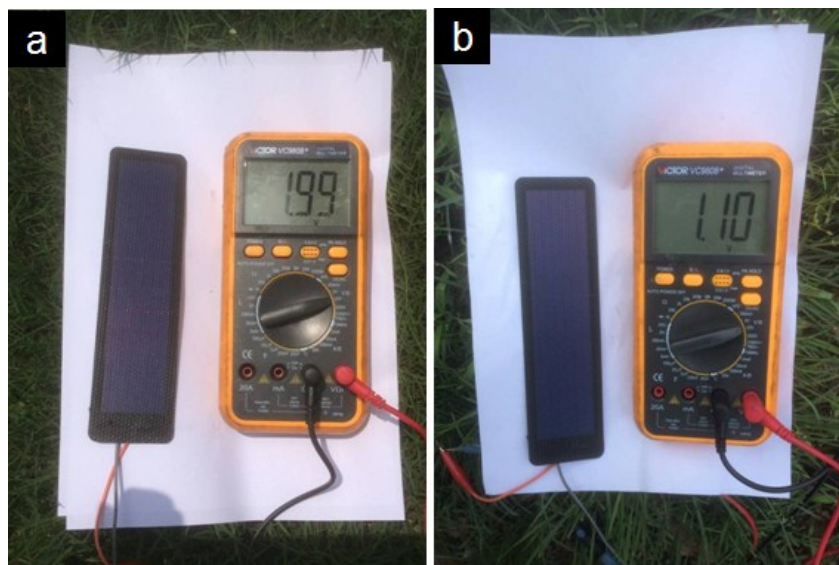


Figure S8. Output voltage of solar cell at different conditions. (a) Noontime with abundant sunshine radiation. **(b)** Afternoon with deficient sunshine radiation.

References

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