Electronic Supplementary Information

Experimental Section

Materials: $Ni(NO_3)_2 \cdot 6H_2O$, hexamethylenetetramine, KOH, NaH_2PO_2, urea and HCl were obtained from Beijing Chemical Corporation. Acetone and ethanol were purchased from Tianjin Chemical Corporation. All chemicals were used as received without further purification. Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. CC was bought from Hongshan District, Wuhan Instrument Surgical Instruments business. The water used throughout all experiments was purified through a Millipore system.

Preparation of NiO NF/CC and Ni_2P NF/CC: In a typical procedure, 5 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 15 mmol hexamethylenetetramine were dissolved in 36 mL distilled water and stirred to form a clear solution. A piece of CC (3 cm × 2 cm) was cleaned by sequential sonication in acetone, ethanol and water several times to remove the surface impurities. Above solution and CC were transferred to a 50 mL Teflon-lined stainless-steel autoclave, which was sealed and maintained at 100 °C for 10 h in an electric oven, and then allowed to cool to room temperature. The resulting CC was rinsed several times with distilled water and ethanol with the assistance of ultrasonication, followed by drying 2 h at 60 ºC, and then annealed at 350 °C in air for 2 h to obtain NiO NF/CC. To prepare Ni_2P NF/CC, NiO NF/CC was placed in the hot center of a tube furnace, and an alumina boat containing 500 mg of NaH_2PO_2 was placed at the farthest upstream position within the tube furnace. Subsequently, the two alumina boats were heated at 300 °C for 2 h with a heating speed of 2 ºC min^{-1} in Ar atmosphere, and then naturally cooled to ambient temperature under Ar. The mass loading of Ni_2P was determined to be 0.92 mg cm^{-2}. The fabrication of CoP NF/CC was similar to Ni_2P NF/CC, except for replacing $Ni(NO_3)_2 \cdot 6H_2O$ with $Co(NO_3)_2 \cdot 6H_2O$.

Preparation of Ni_2P NFs/GCE: Pure Ni_2P NFs were synthesized by the same way without the presence of CC. In a typical procedure, the glassy carbon electrode

(GCE, diameter 3 mm) was respectively polished with 1, 0.3, and 0.05 μm alumina slurry and cleaned by brief ultrasonication. Then cleaned electrode was dried under nitrogen flow. 2 mg Ni_2P NFs were dispersed in 20 μL 5 wt% Nafion solution and 980 μL of aqueous ethanol solution (1:1). The Ni_2P NFs modified GCE (Ni_2P NFs/GCE) was prepared by casting 10.35 μL of Ni_2P NFs suspension (2 mg mL^{-1}) on a GCE surface and dried in air as working electrode.

Preparation of Pt/C and RuO_2 loaded electrodes: RuO_2 catalyst was prepared as follows. In brief, 0.01 mol $RuCl_3 \cdot 3H_2O$ was dissolved in 100 mL deionized water and heated at 100 °C for 10 min, followed by the addition of 1 mL 1.0 M KOH solution. The reaction mixture was maintained at 100 °C under stirring for 45 min. After that, the solution was centrifuged for 10 minutes and filtered. The precipitate was washed several times with deionized water to remove the remaining chlorides. The resulting Ru-hydroxide was dried for 5 h at 80 °C and then calcined in air at 300 °C for 3 h to obtain RuO_2. To prepare Pt/C and RuO_2 loaded electrodes, 20 mg Pt/C or RuO_2 and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30-min sonication to form an ink finally. Then 46 μL catalyst ink was loaded on bare CC with a catalyst loading of 0.92 mg cm^{-2}.

Characterizations: XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) using a three-electrode system with Ni_2P NF/CC, graphite plate, and saturated calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s^{-1}. All tests were carried out at room temperature.

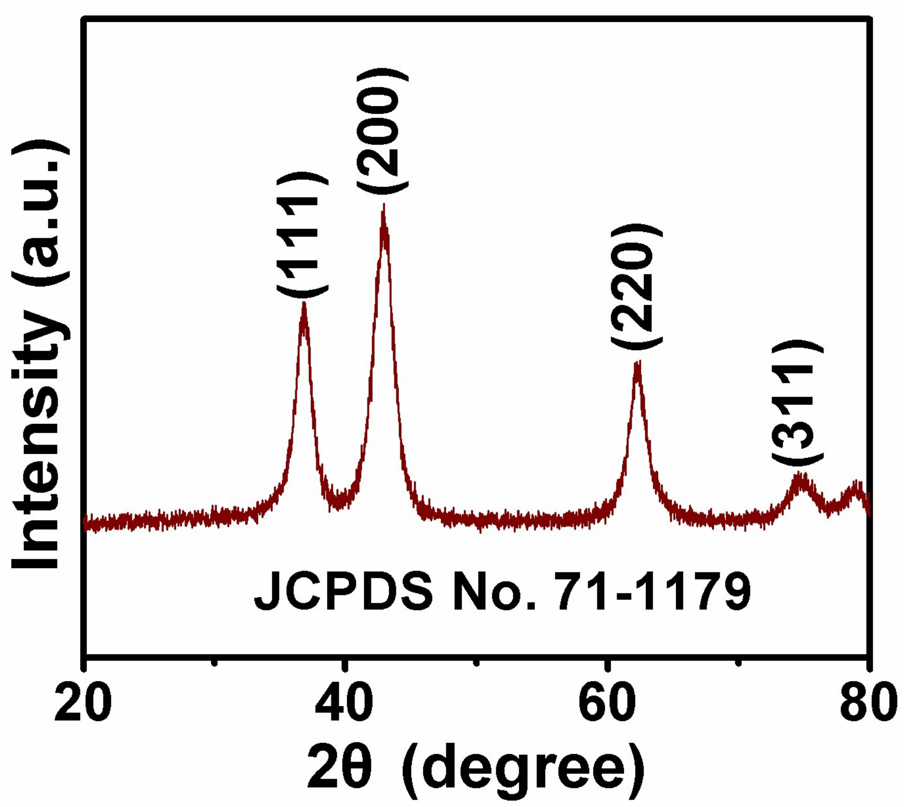

Fig. S1. XRD pattern of Ni_2O.

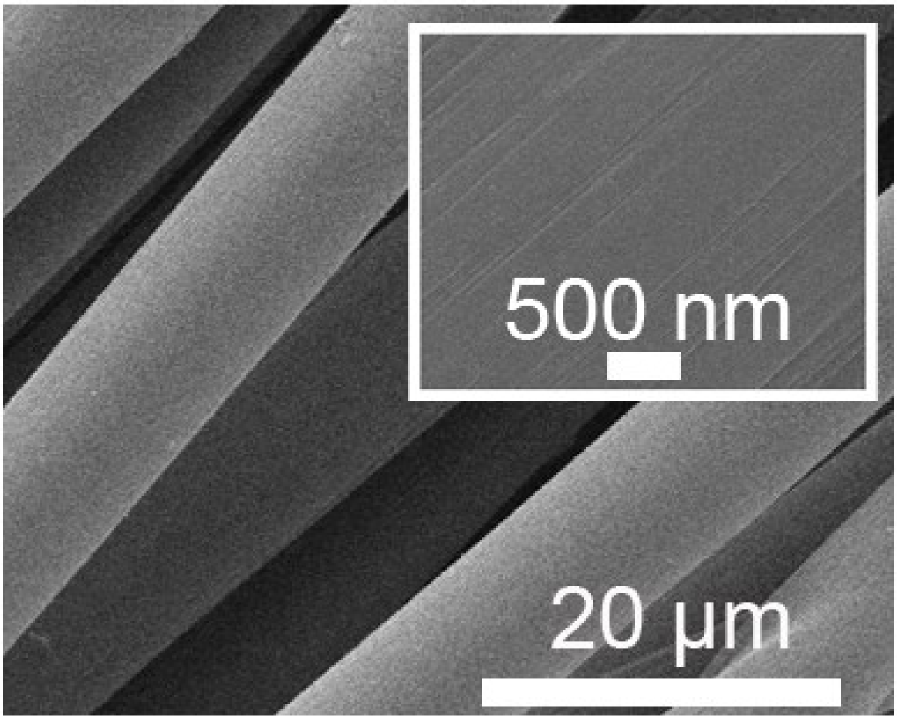

Fig. S2. SEM images of bare CC.

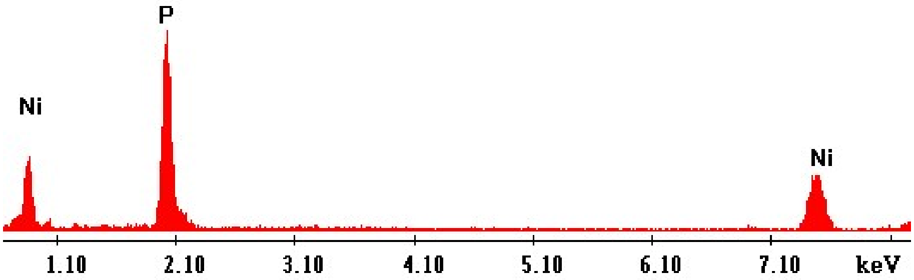

Fig. S3. EDX spectrum of Ni_2P NF/CC.

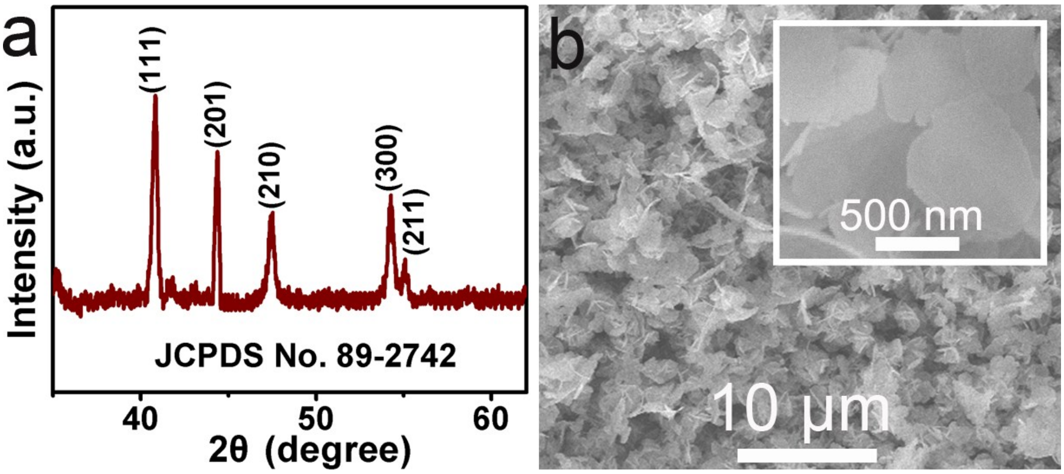

Fig. S4. (a) XRD pattern of Ni_2P NFs. (b) SEM images of Ni_2P NFs.

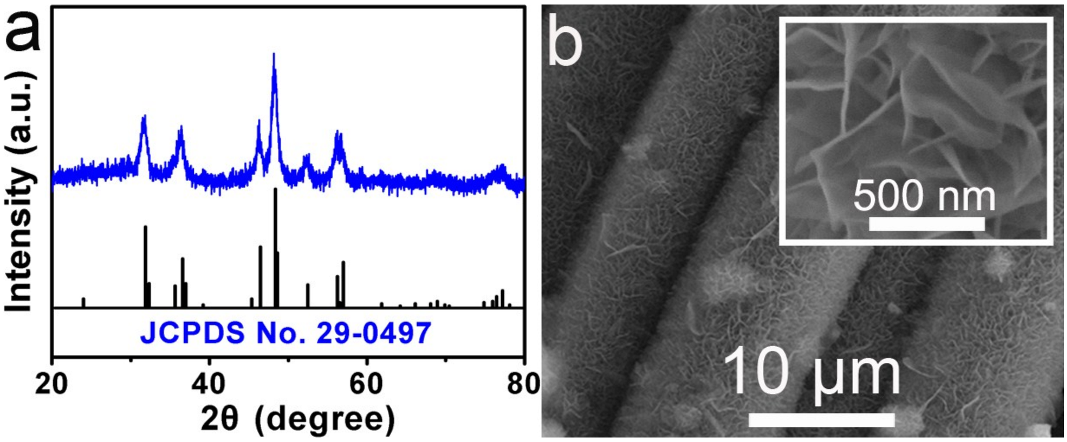

Fig. S5. (a) XRD pattern of CoP nanoflakes. (b) SEM images of CoP NF/CC.

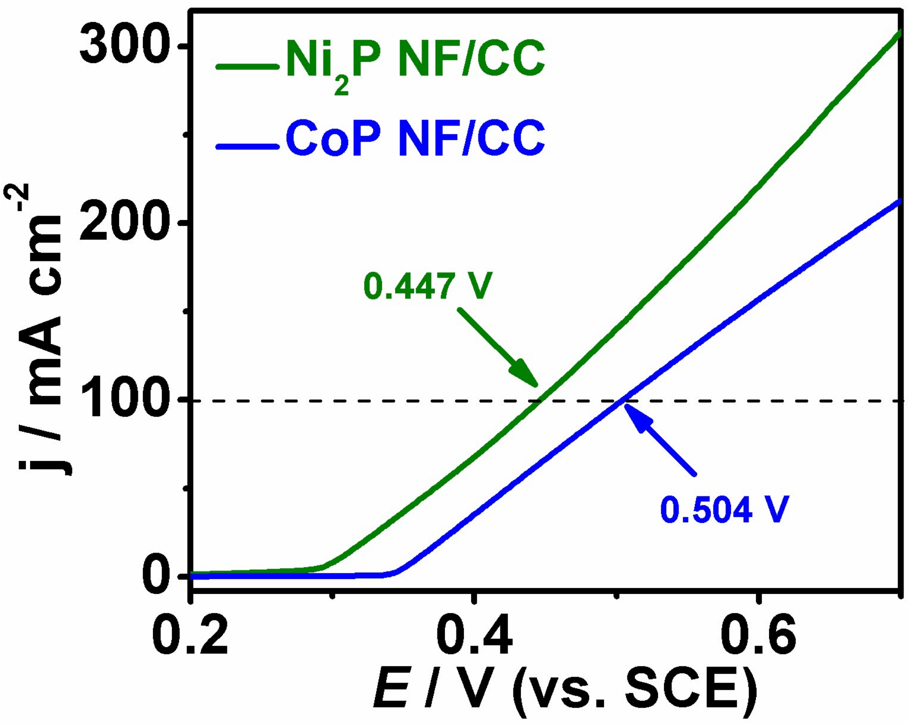

Fig. S6. LSV curves of Ni_2P NF/CC and CoP NF/CC in 1.0 M KOH with 0.5 M urea at a scan rate of 5 mV s^{-1}.

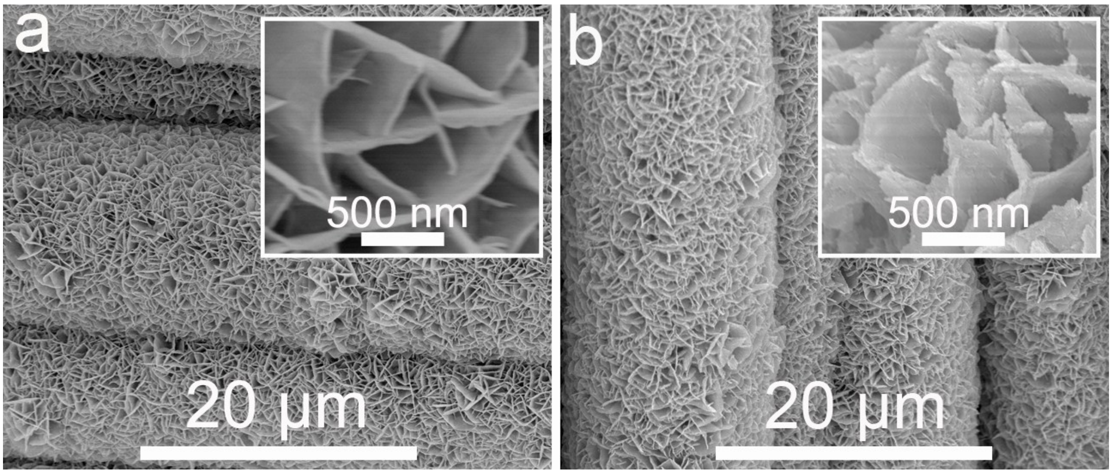

Fig. S7. SEM images for Ni_2P NF/CC after HER (a) and UOR (b) electrolysis.

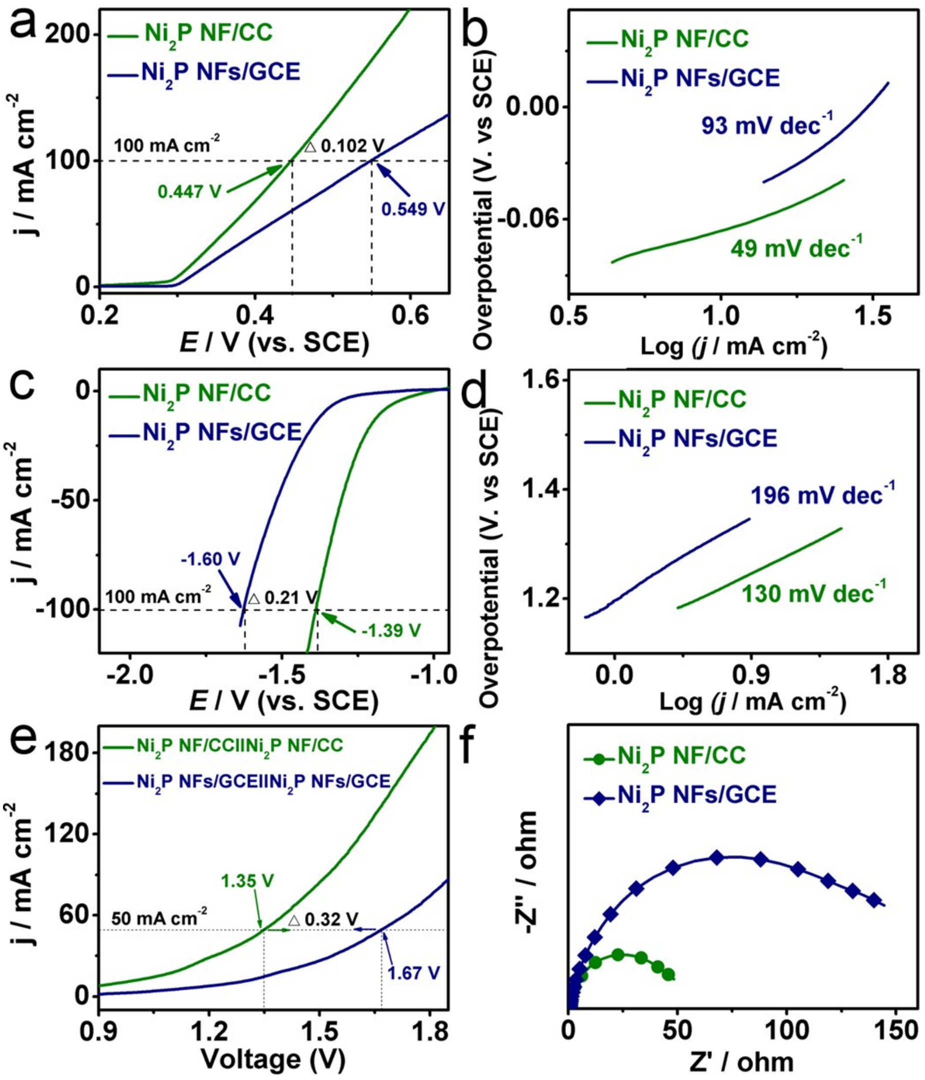

Fig. S8. (a) LSV curves of Ni_2P NF/CC and Ni_2P NFs/GCE in 1.0 M KOH with 0.5 M urea at a scan rate of 5 mV s^{-1}. (b) Tafel plots for Ni_2P NF/CC and Ni_2P NFs/GCE. (c) LSV curves of Ni_2P NF/CC and Ni_2P NFs/GCE in 1.0 M KOH with 0.5 M urea at a scan rate of 5 mV s^{-1}. (d) Tafel plots for Ni_2P NF/CC and Ni_2P NFs/GCE. (e) Polarization curves for Ni_2P NF/CC||Ni_2P NF/CC and Ni_2P NFs/GCE||Ni_2P NFs/GCE in 1.0 M KOH with 0.5 M urea at scan rate of 5 mV s^{-1}. (f) Nyquist plots for Ni_2P NF/CC and Ni_2P NFs/GCE.

Movie S1. This movie shows vigorous evolution of gas bubbles on Ni_2P NF/CC electrodes in a two-electrode setup driven by 1.10 V in 1.0 M KOH with 0.5 M urea.