Supporting information:

Morphology-Controllable Synthesis of Cobalt Telluride Branched Nanostructures on Carbon Fiber Paper as Electrocatalysts for Hydrogen Evolution Reaction

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Experimental:

Preparation

All chemicals used in our experiments are of analytical grade without further purification. Ultrapure water (electrical resistance ≈ 18.2 MΩ cm) was used throughout our experiments.

The synthesis of $CoTe_2$ NDs/$CoTe_2$ NTs and CoTe NSs/$CoTe_2$ NTs could be divided into two different steps: (1) hydrothermal synthesis of $Co(OH)(CO_3)_{0.5}$ NWs on CFP and (2) conversion of the $Co(OH)(CO_3)_{0.5}$ NWs to $CoTe_2$ NDs/$CoTe_2$ NTs and CoTe NSs/$CoTe_2$ NTs structures via an conversion reaction.

In step 1, the commercially available CFP, TGH-060 (Toray Industries, Inc.) was cut into pieces of 10×60 cm^2 in advance. Then the pieces of CFP were ultrasonically washed by ethanol and 0.1 M H_2SO_4 solution as well as water in sequence. Meanwhile, the 0.87 g $Co(NO_3)_2\cdot6H_2O$ (Aladdin), 0.90 g $CO(NH_2)_2$ (Sinopharm Chemical Reagent CO., Ltd.) and 0.22 g NH_4F (Aladdin) were dissolved by 80 mL ultrapure water. The solution was then transferred into a 100 ml Teflon-lined stainless steel autoclave and the CFP was deposited and immersed by the solution. After being tightly sealed, the autoclave was heated in an electrical oven at 120 °C for 7 h. The product of hydrothermal process was taken out and washed by water and ethanol for several times. After drying at 80 °C, $Co(OH)(CO_3)_{0.5}$ NWs on CFP were successfully prepared.[1-2]

In step 2, for the synthesis of $CoTe_2$ NDs/$CoTe_2$ NTs, 2 mM Na_2TeO_3 (Aladdin) was added into a Teflon autoclave and dissolved by 70 ml water. Then 10 ml 98% (T) $N_2H_4\cdot H_2O$ (Aladdin) was added into the solution under vigorous stirring. The prepared $Co(OH)(CO_3)_{0.5}$ NWs on CFP were then transferred into the homogeneous solution. In the case of synthesizing CoTe NSs/$CoTe_2$ NTs, a similar process was taken except for adding 2 mM Te powder (Sigma Aldrich) and 8 mM $NaBH_4$ instead of Na_2TeO_3 and $N_2H_4\cdot H_2O$ into 80 ml water. The tightly sealed autoclaves were placed in an electric oven and kept at 180 °C for 15 h. After cooling down naturally and washed by water and ethanol, the samples were dried in vacuum for 2 h. As control group, the CoTe NTs grown on CFP were prepared according to Patil's work with reaction temperature of 20 °C for 15 h.[3]

Characterization

An X-ray diffractometer (XRD, PANalytical X'pert Pro) was used to identify the crystal structure. The X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) was conducted to characterize the electronic structure and oxidation state information. The morphologies of our cobalt telluride branched nanostructures were observed with a scanning electron microscope (SEM, Hitachi SU 6600). The detailed morphologies and crystal structures were investigated with a high-resolution transmission electron microscope (HRTEM, JEOL JEM 2100F) equipped with the scanning transmission electron microscope (STEM). The element distribution and atom ratios were identified by energy dispersive X-ray spectroscopy (EDS, Oxford Instrument and EDAX Inc.). The loadings of active materials were obtained with a high-precision electronic balance (0.01 mg, Sartorius BT25s). The loading of $Co(OH)(CO_3)_{0.5}$ NWs was ~1.6 mg cm^{-2} and the loadings of $CoTe_2$ NDs/$CoTe_2$ NTs and CoTe NSs/$CoTe_2$ NTs were similar, with the figures of 4.57 and 4.85 mg cm^{-2} respectively.

Electrochemical evaluation

0.5 M H_2SO_4 solution was purchased from Aladdin and directly used as electrolyte. All the electrochemical evaluations were performed on an electrochemical workstation (CHI 660D, CH Instruments, Inc.) in a 3-electrode configuration. Highly pure nitrogen gas was bubbled into the electrolyte throughout the evaluation process. Our samples were cut into 20×10 mm^2 piece in advance and the geometric area of 10×10 mm^2 as working electrode was defined with electrochemically inert silicon rubber. A highly pure graphite rod (99.9995% Alfa Aesar) was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The reference electrode was calibrated in the hydrogen saturated electrolyte using two Pt wires (Ø 0.5 mm, 3.5N, Sinopharm Chemical Reagent CO., Ltd.) as working and counter electrodes respectively. The potential shift of the SCE was determined to be -0.266 V vs RHE. Linear sweeping voltammetry (LSV) conducted from 0.2 to -0.6 V (vs

RHE) at a scan rate of 5 mV s^{-1} was measured to identify the overpotential needed to produce hydrogen. Cyclic voltammetry (CV) was performed at the scan rates of 10, 20, 50, 100, 200 mV s^{-1} within the scan range from 0.1 to 0.2 V (vs RHE) to determine the double-layer capacitance. The electrochemical impedance spectroscopy (EIS) was conducted at -0.15 V (vs RHE) with an amplitude of 10 mV ranging from 100 k to 1 Hz. The cycling performance was measured by conducting 5000 cycles of CV within the potential range from 0.2 V (vs RHE) to the overpotential driving the initial current density of ~20 mA cm^{-2}. The stability was also characterized by performing a continual electrolysis for 20 h at the overpotential delivering an initial current density of ~50 mA cm^{-2}. The series resistances (R_s) were derived from x-axis intercepts of Nyquist plots and the charge transfer resistances (R_{ct}) were determined by fitting the EIS data with an equivalent circuit. As a compare group, commercially available Pt/C (20 wt% Pt on Vulcan XC-72R, Sigma-Aldrich) of the similar loading with cobalt telluride branched nanostructure was ultrasonically mixed with 5 μl 5% Nafion solution and 200 μl absolute ethanol and then drop cast onto the CFP with an active area of 10×10 mm^2 acting as working electrode.

***IR*-correction**

All the data in polarization curves and corresponding Tafel plots have been *iR*-corrected. The *iR*-correction is to subtract the potential loss caused by the R_s from the raw potential data, where the potential loss is calculated by the Ohm's law. The series resistances (R_s) were derived from x-axis intercepts of Nyquist plots. The R_s of $CoTe_2$ NDs/$CoTe_2$ NTs, CoTe NSs/$CoTe_2$ NTs and CoTe NTs are 2.13, 1.95 and 1.81 Ω respectively. The low and consistent R_s testifies the reliability of comparisons of our samples and also improves the credibility of our data. The example of *iR*-correction for the polarization curve of the CoTe NSs/$CoTe_2$ NTs is presented in Fig. S5.

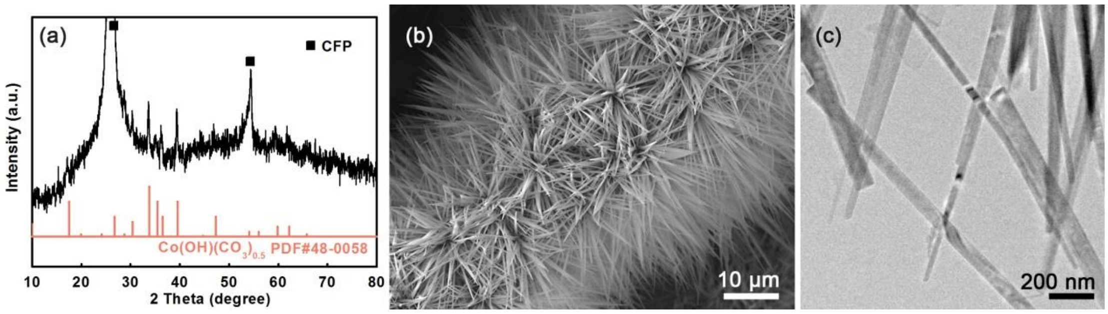

Fig. S1. (a) The XRD pattern of $Co(OH)(CO_3)_{0.5}$ NWs grown on CFP. (b) SEM and (c) TEM images of $Co(OH)(CO_3)_{0.5}$ NWs.

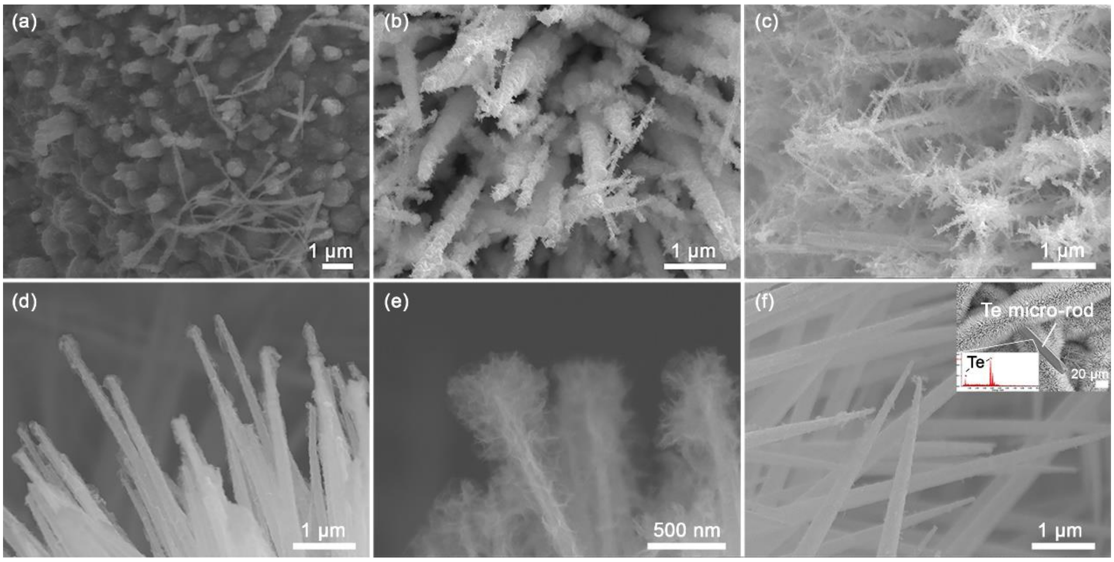

Fig. S2. $CoTe_2$ NDs/$CoTe_2$ NTs synthesis with (a) 0.5 mM Na_2TeO_3 and 10 mL $N_2H_4{\cdot}H_2O$, (b) 1 mM Na_2TeO_3 and 10 mL $N_2H_4{\cdot}H_2O$ and (c) 2 mM Na_2TeO_3 and 10 mL $N_2H_4{\cdot}H_2O$; CoTe NSs/$CoTe_2$ NTs synthesis with (d) 1 mM Te powder and 4 mM $NaBH_4$, (e) 2 mM Te powder and 8 mM $NaBH_4$ and (f) 3 mM Te powder and 12 mM $NaBH_4$. The inset of (f) gives the morphology of Te micro-rod and its corresponding EDS spectrum.

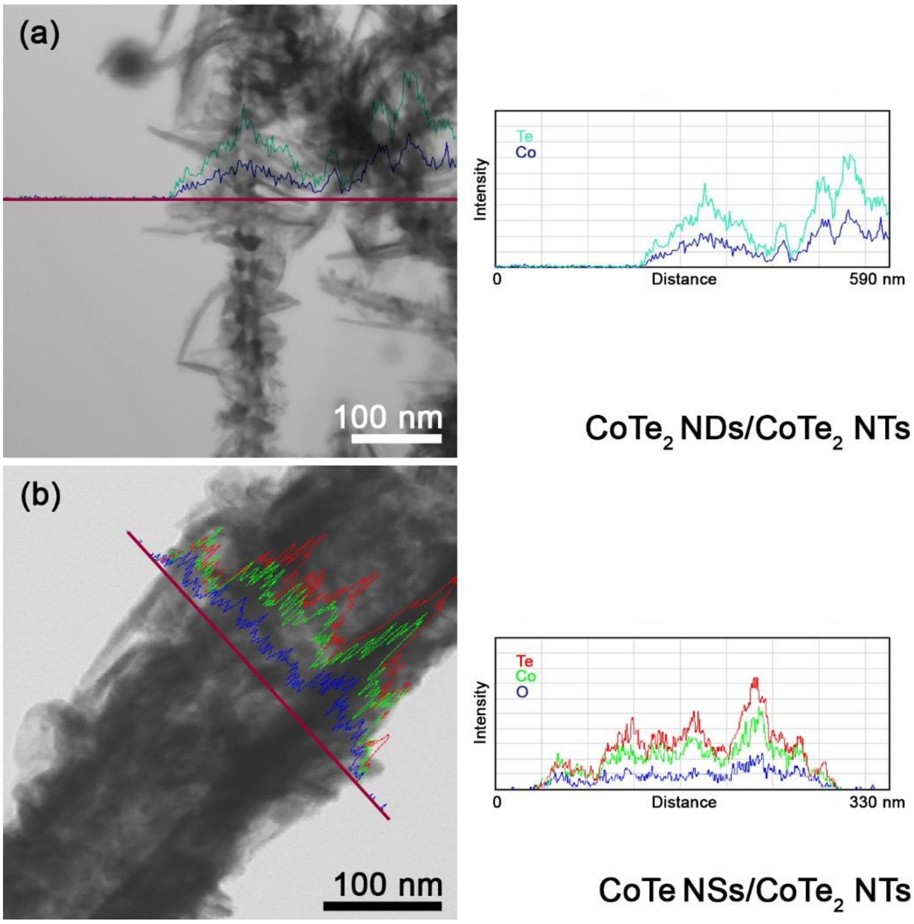

Fig. S3 EDS line-scan analysis of (a) $CoTe_2$ NDs/$CoTe_2$ NTs and (b) CoTe NSs/$CoTe_2$ NTs

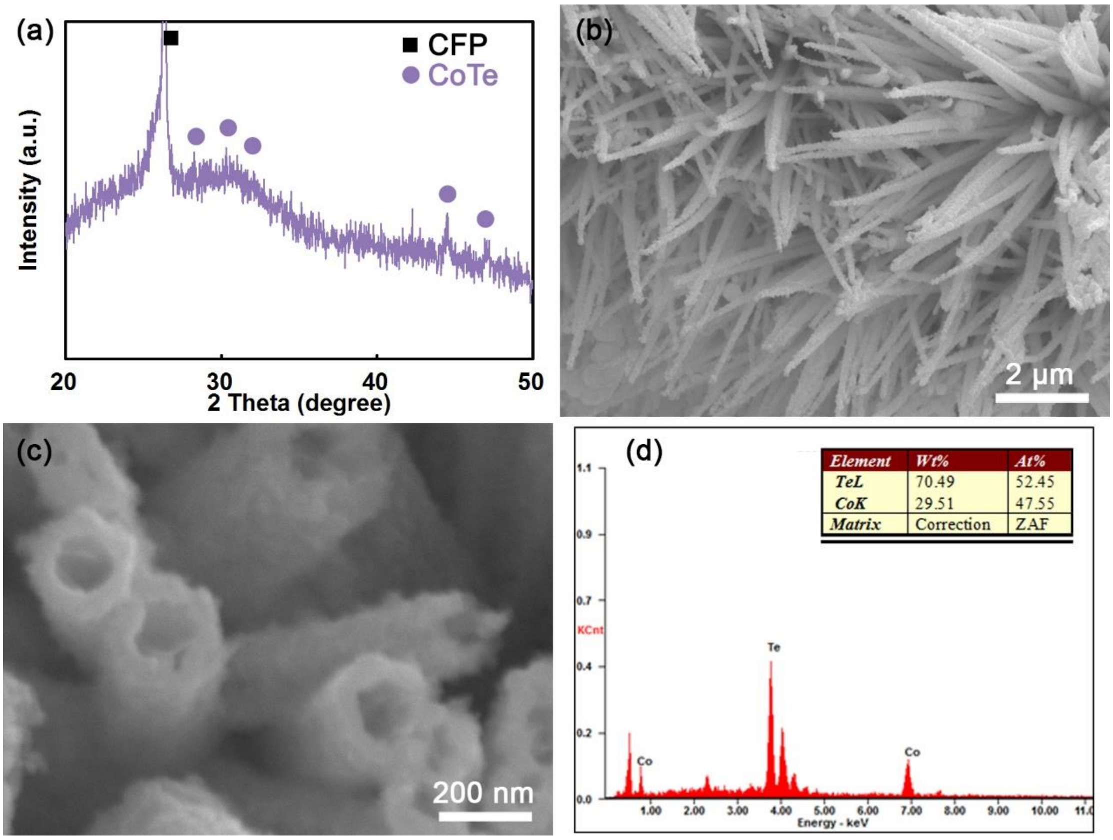

Fig. S4 (a) XRD pattern of CoTe NTs grown on CFP. SEM images of (b) CoTe NTs and (c) some broken ones. (d) The corresponding EDS spectrum of CoTe NTs on CFP with the Co to Te atom ratio being nearly 1: 1.

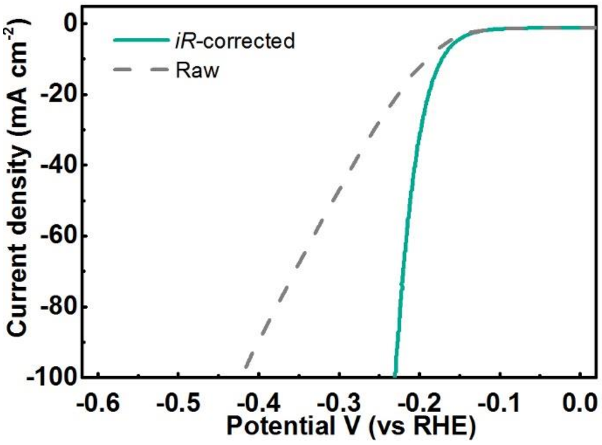

Fig. S5. The polarization curves of CoTe NSs/CoTe$_2$ NTs before and after *iR*-correction.

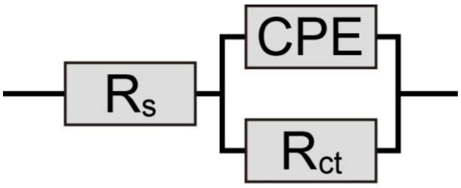

Fig. S6. The equivalent circuit used in the simulation of Tafel plots.

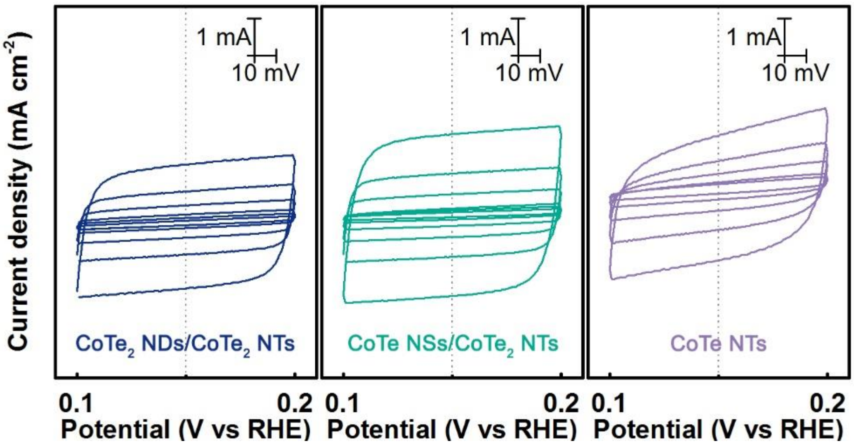

Fig. S7. CV curves of CoTe$_2$ NDs/CoTe$_2$ NTs, CoTe NSs/CoTe$_2$ NTs and CoTe NTs.

References:

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