1   **Electronic Supplementary Information**

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3   **Directly Electro-Catalyze Crude Syngas to Ethylene via a Multi-**

4   **Process Coupled Device**

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Experimental Section

Chemicals

$Co(NO_3)_3 \cdot 6H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, urea, citric acid and ethylene glycol (99.8%) were purchased from Sigma-Aldrich. $CuSO_4 \cdot 5H_2O$, L-ascorbic acid, ethanol, NaOH, NaCl and polyvinyl pyrrolidone K-30 (PVP) were purchased from Sinopharm Chemical Reagent Co., Ltd. $Na_2S \cdot 6H_2O$ were purchased from Xilong Scientific Co., Ltd. All chemicals were used as received without further purification.

Preparation of CoNi@NGs and CoNiO$_x$-CNTs

The CoNi@NGs were prepared through a template-assisted method.[1] Briefly, Co and Ni precursor were precipitated on the SiO_2 templet by the hydrothermal method. Then transfer the gotten sample into a CVD furnace, and deposit graphene shells by bubbling CH_3CN as the carbon and nitrogen source at 600 °C. Finally, the samples CoNi@NGs were collected after washed in HF aqueous solution and distilled water. For CoNiO$_x$-CNTs preparation, the Co and Ni precursor were firstly precipitated on the carbon nanotubes (CNTs) via the hydrothermal method, and then the sample was treated at 400 °C under Ar for 1 h in the CVD furnace.

Preparation of Cu catalyst

For synthesis of Cu catalyst, $CuSO_4 \cdot 5H_2O$, PVP and NaCl were dissolved by ethylene glycol (EG) in a flask. Then the mixture of NaOH and L-ascorbic acid EG solution was preheated was injected to the flask for 40 minutes in the heating of 100 °C. The Cu catalyst was collected by centrifuge and washed with deionized H_2O and ethanol, respectively. The obtained Cu sample was dispersed into ethanol and used for preparing cathodic electrode for CO electroreduction.[2]

Characterization

Transmission electron microscope (TEM) was conducted on Tecnai F20

47   transmission electron microscope operated at an accelerating voltage of 200 kV.

48   Scanning electron microscopy (SEM) measurements were carried out by using Hitachi

49   S-4800 scanning electron microscope with 15 kV accelerating voltage. The Faradic

50   efficiency (FE) of gas phase products was measured on gas chromatography GC 2060

51   produced by Ruimin Instrument Company in Shanghai. The FE of liquid phase products

52   was analyzed on a Bruke 500-MHz NMR spectrometer. The content of H_2S was

53   confirmed by Quadrupole Mass Spectrometer EQMS-I (Shanghai Quan Tang Scientific

54   Instruments).

55

56   **Electrochemical measurements**

57   All the electrochemical measurements were carried out with CHI 760E equipped

58   with a gas flow controlling system at 25 $^{\circ}$C. The test was carried in a double-cell

59   electrolytic tank segregated with Nafion 117 membrane. The electrodes were set in the

60   1 M NaOH electrolyte.

61

62   **Preparation of the anodic electrode**

63   The anodic electrode was assembled by covering CoNi@NGs catalyst on a Ni

64   foam electrode (1 cm^2 square, 1 mm thickness). Typically, 7 mg CoNi@NGs catalyst

65   was dispersed in 1.95 mL ethanol with 50 uL Nafion solution (5 wt%, Du Pont) to form

66   a homogeneous ink. Then 2 mL ink was added dropwise onto the Ni foam and dried

67   under the room temperature. The final loading of CoNi@NGs was 7 mg cm^{-2}.

68

69   **Preparation of the cathodic electrode**

70   The carbon paper (GDS3250) with micro-porous layer (MPL) was bought from

71   *AvCarb Material Solutions*. For preparing electrode loading catalysts, 10 mg catalysts

72   and 50 μL Nafion solution were dispersed into 1.5 mL ethanol by ultrasound. Then the

73   ink was dropped on the carbon papers and dried under the room temperature. The final

74   loading of Cu particles was 1 mg cm^{-2}.

75

The SOR catalytic performance test of CoNi@NGs

For SOR reaction, 1 M Na_2S was added in the anodic electrolyte. The polarization curve of CoNi@NGs was tested in a standard three-electrode cell. The reference electrode Hg/HgO was calibrated according to the formula $E_{versus\ RHE} = 0.098 + 0.0591$ pH. The pH was tested by the pH value meter at 25 ℃. The activities of CoNi@NGs were evaluated with a scan rate of 5 mV/s. The test of galvanostatic method was tested in a standard two-electrode cell. The catalytic performance of direct electrolysis of H_2S-contained syngas was performed after bubbling the H_2S-contained syngas to the anodic electrolyte for one hour.

The CORR catalytic performance of Cu catalyst

The performance of Cu catalyst in the coupled device was measured by the galvanostatic method. The FE of gas phase and liquid phase products was measured by gas chromatography and NMR spectrometer, respectively.

Gas chromatography and NMR analysis

The amount of H_2 and C_2H_4 was evaluated by gas chromatography. During the test, reaction gas (CO or syngas) was purged continuously through the mass flow meter and directly routed into gas chromatography every 10 min. Quantification of the H_2 and C_2H_4 were performed using the thermal conductivity detector (TCD) and flame ionization detector (FID), respectively. The quantity and retention time of the gas were calibrated with a series of standard gas samples. The FEs of cathodic gas products were calculated by the following equation:

$$R_{product} = \frac{A_{test}}{A_{standard}} \times c_{standard} \times R_{reaction\ gas}$$

$$i_{product} = R_{product} \times \frac{2Fp_0}{RT}$$

$$FE_{product} = \frac{i_{product}}{i_{total}} \times 100\%$$

$R_{product}$: flow rate of H_2 or C_2H_4

A_{test} : peak area of the gas generated at the specific time point

104     $A_{standard}$: peak area of the gas in the standard gas samples

105     $c_{standard}$: volume concentration of test gas in the standard gas samples

106     $R_{reaction\ gas}$: flow rate of reaction gas

107     $i_{product}$: geometric current density of H_2 or C_2H_4

108   F : Faradic constant, 96485 C mol^{-1}

109   p_0 : pressure

110   R : ideal gas constant, 8.314 J mol^{-1} K^{-1}

111   T : temperature, 298 K

112     $FE_{product}$: Faradic efficiency of H_2 or C_2H_4

113   i_{total} : total current density in the reaction

114   The liquid products were analyzed on a Bruke 500-MHz NMR spectrometer. The

115 0.5 mL sample of the electrolyte was mixed with 0.05 mL D$_2$O and 0.05 mL 2.38 mM

116 dimethyl sulphoxide (DMSO, used as internal standard). The one-dimensional ^{1}H

117 spectrum was measured with water suppression method. The amount of products were

118 calculated according to standard curves, which were tested by a series of standard gas

119 samples.

120   There are four carbon-based products in the cathode from CORR. The selectivity

121 of C$_2$H$_4$ was were calculated by the following equation:

122
$$FE_{CORR} = FE_{C_2H_4} + FE_{EtOH} + FE_{AcO^-} + FE_{n-Pro}$$

123
$$S_{C_2H_4} = \frac{FE_{C_2H_4}}{FE_{CORR}}$$

124   FE_{CORR} : The cathodic FE of CO reduced reaction

125     $S_{C_2H_4}$: The selectivity of C$_2$H$_4$

126

127 **Energy saving efficiency analysis**

128 The value of energy saving efficiency was calculated to verify the low energy

129 consumption of ethylene production in the coupled device versus uncoupled device.

130 The energy saving efficiency is calculated based on the following equations:

131
$$E_{device} = U \times I \times t$$

132 $$E_u \, or \, E_c = \frac{E_{device} \times FE_{C_2H_4}}{n_{C_2H_4}}$$

133 $$Energy \, Saving \, efficiency_{C_2H_4} = \frac{E_u - E_c}{E_u} \times 100\%$$

134 E_{device} : the energy consumption of the device

135 U : the applied potential for the device

136 I : the applied current for the device

137 t : reaction time

138 $E_u \, or \, E_c$: the energy consumption of ethylene production in the uncoupled device (E_u)

139 or coupled device (E_c)

140 $n_{C_2H_4}$: the amount of produced C_2H_4

141 $Energy \, Saving \, efficiency_{C_2H_4}$: the energy saving efficiency in the multi-process

142 coupled device

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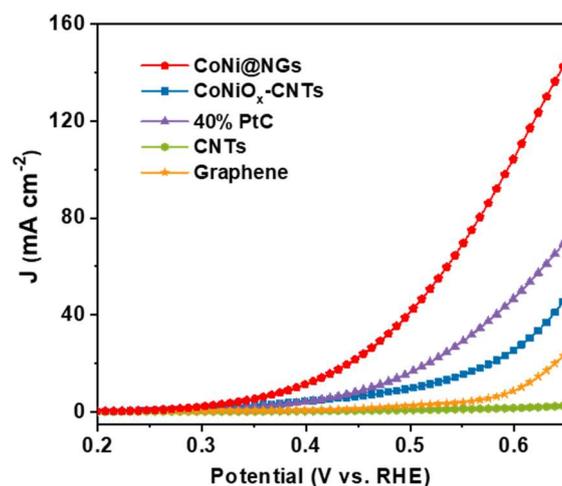
144

145 **Fig. S1** The SOR polarization curves for CoNi@NGs in comparison with 40% Pt/C,

146 graphene, carbon nanotubes (CNTs) and the cobalt and nickel oxide nanoparticles

147 supported on carbon nanotubes (CoNiO$_x$-CNTs) at the same mass loading. The current

148 density of CoNi@NGs is much higher than the other materials, which indicates that

149 CoNi@NGs possess a higher activity for H$_2$S oxidation. The mixture of 1 M NaOH and

150 1 M Na$_2$S serves as the anodic electrolyte and 1 M NaOH serves as the cathodic

151 electrolyte.

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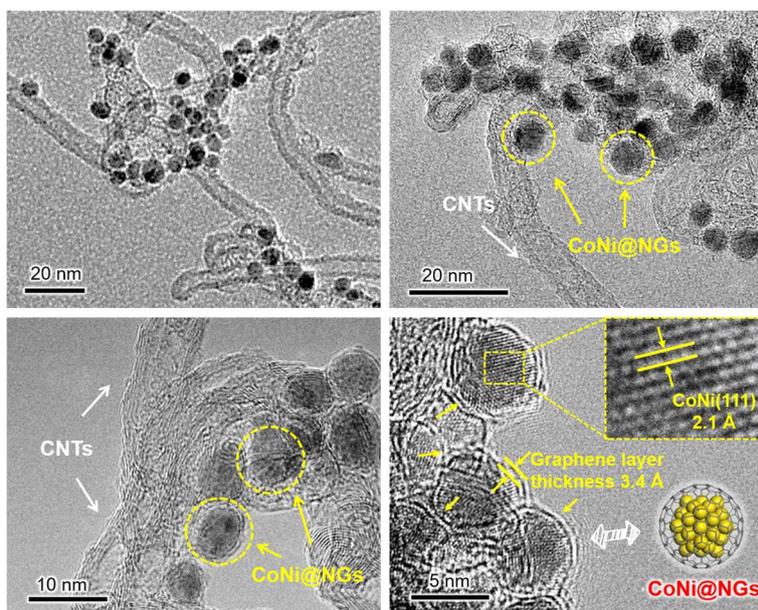
153

154 **Fig. S2** The TEM images of CoNi@NGs. It clearly shows that the CoNi alloy

155 nanoparticles are encapsulated by the single layer graphene.

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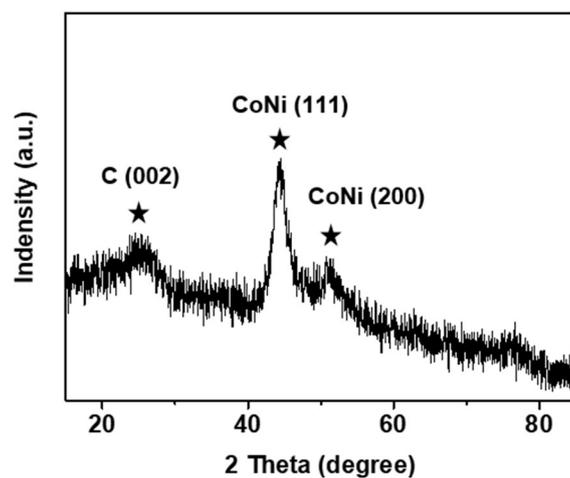
Fig. S3 The X-ray diffraction (XRD) pattern of CoNi@NGs. The crystal structure of CoNi alloy NPs is confirmed by the XRD test, which exhibits two main diffraction peaks at $2\theta = 44.44°$, and $51.72°$, corresponding to the (111) and (200) facets of the CoNi alloy.

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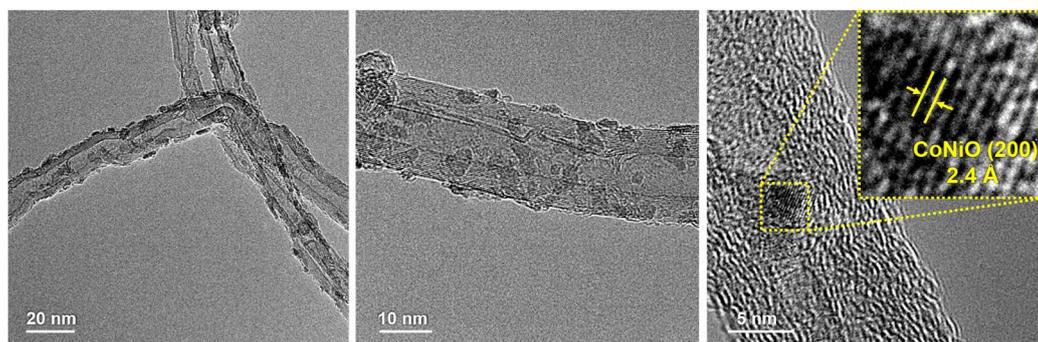
Fig. S4 The HRTEM images of $CoNiO_x$-CNTs. The cobalt and nickel oxide nanoparticles ($CoNiO_x$) are supported on the CNTs evidenced by the crystal plane of CoNiO(200).

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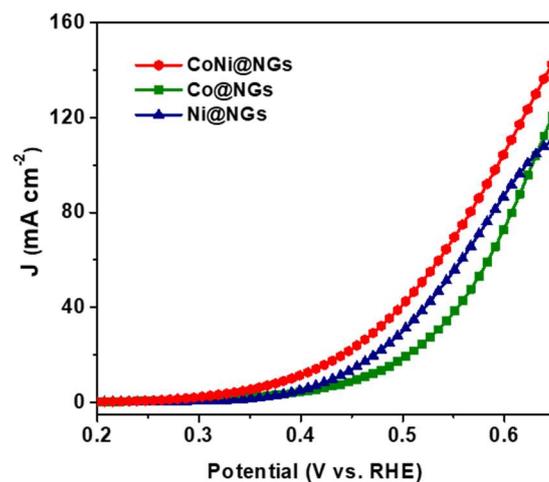
168

169 **Fig. S5** The SOR polarization curves for CoNi@NGs in comparison with Co@NGs,

170 Ni@NGs at the same mass loading. The current density of CoNi@NGs is much higher

171 than the Co@NGs and Ni@NGs. The mixture of 1 M NaOH and 1 M Na_2S serves as

172 the anodic electrolyte and 1 M NaOH serves as the cathodic electrolyte.

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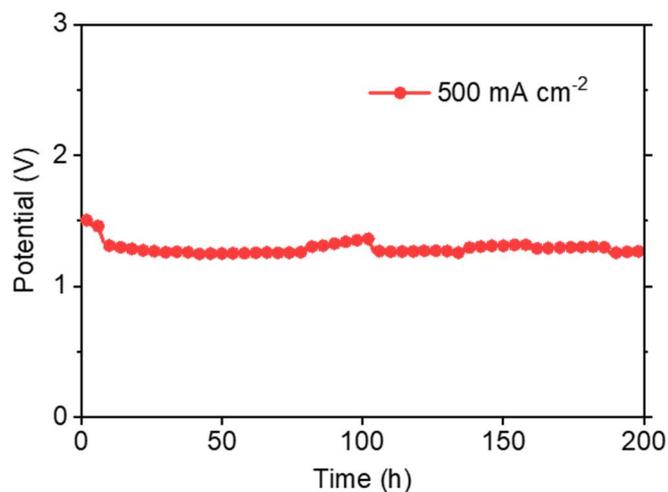
174

175 **Fig. S6** Galvanostatic test for the CoNi@NGs in the SOR at the current density of 500

176 mA cm^{-2} for 200 hours.

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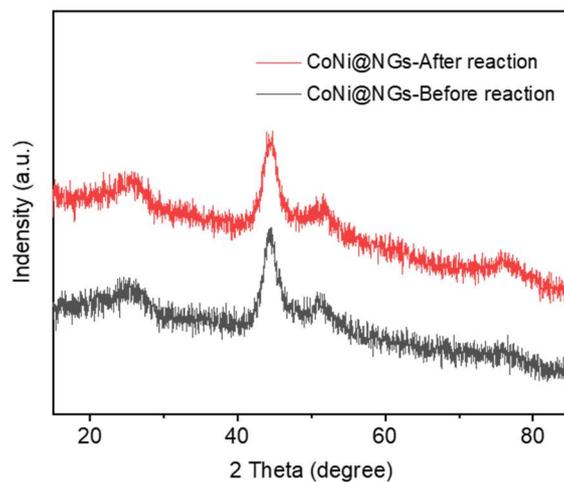
Fig. S7 The X-ray diffraction (XRD) pattern of CoNi@NGs before and after 200 hours'

180 durability test.

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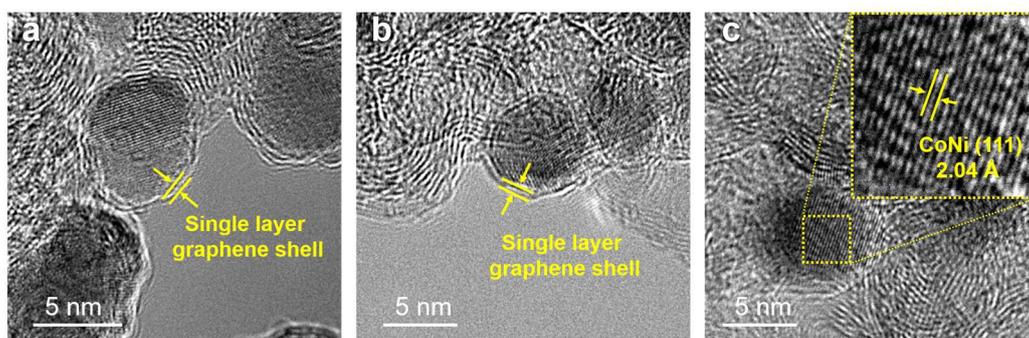
Fig. S8 The HRTEM images of CoNi@NGs after 200 hours' durability test.

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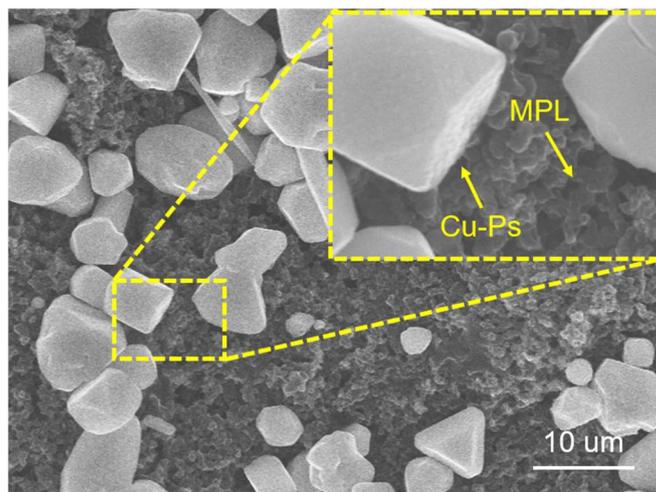
Fig. S9 The SEM image of Cu catalyst electrode. The Cu particles were loaded on the

carbon paper with micro-porous layer.

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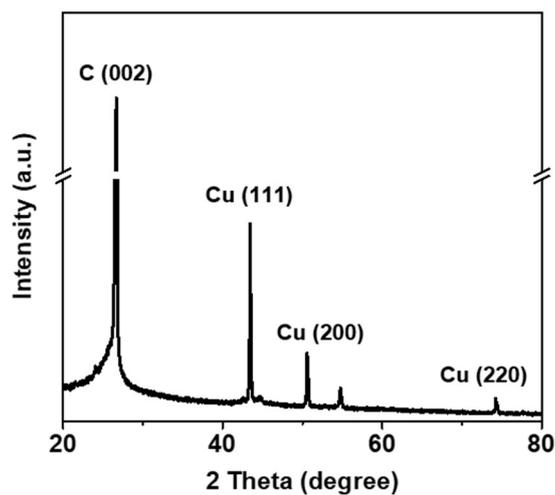
Fig. S10 The XRD pattern of Cu catalyst. The crystal structure of Cu presents three

main diffraction peaks, corresponding to the (111), (200) and (220) facets of the Cu foil.

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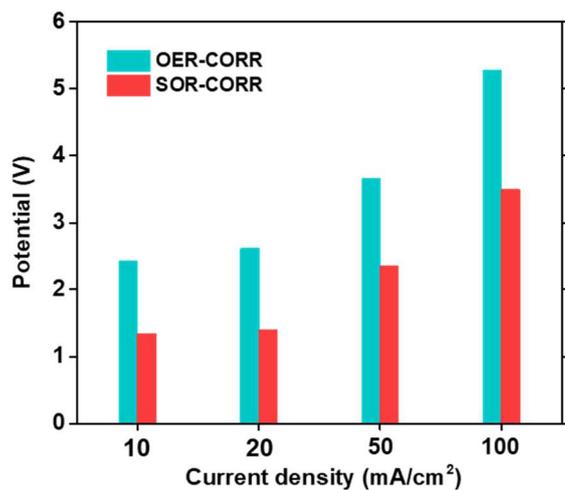
Fig. S11 Comparison of the potentials for SOR-CORR and OER-CORR at the current density of 10, 20, 50 and 100 mA cm^{-2}.
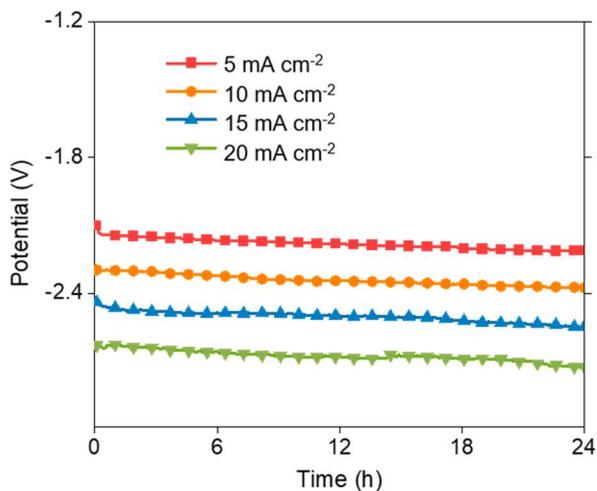
Fig. S12 Galvanostatic test for the uncoupled device in the OER-CORR process at the current density from 5 to 20 mA cm^{-2} in 24 hours.

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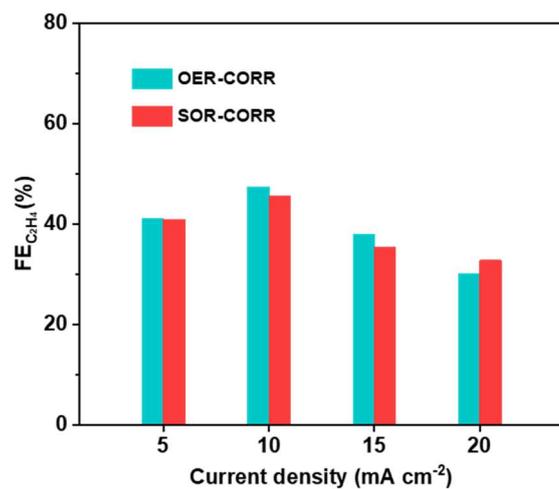
Fig. S13 The comparison of FE for ethylene production in the SOR-CORR process and the OER-CORR process.

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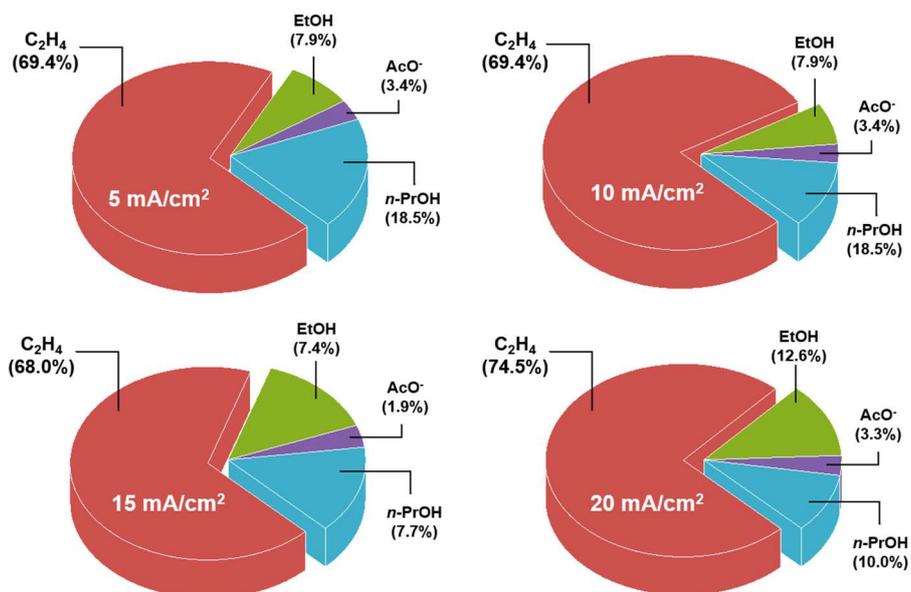
Fig. S14 The selectivity of CORR at the current density from 5 to 20 mA cm^{-2}.

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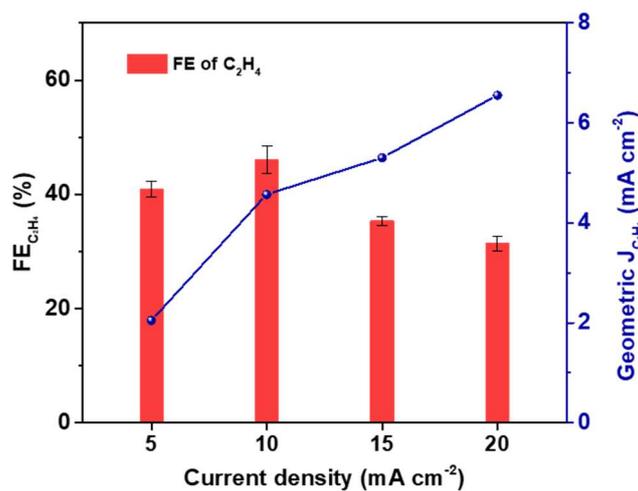
Fig. S15 The geometric current density for CO electroreduction to C_2H_4 production in

the two-electrode SOR-CORR reaction.

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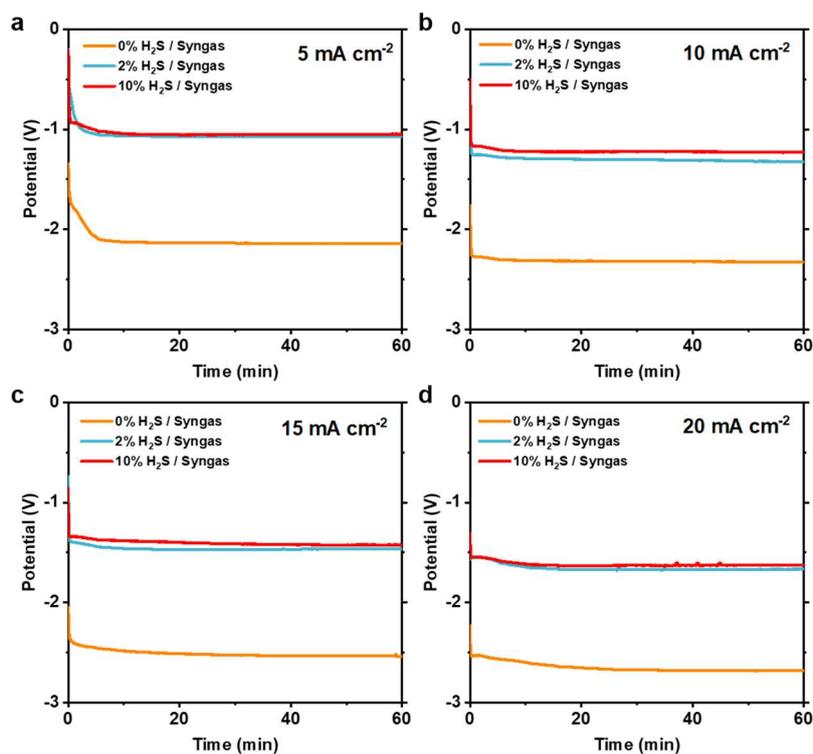
Fig. S16 The potentials of the coupled device at different current densities when dealing

with different syngas.

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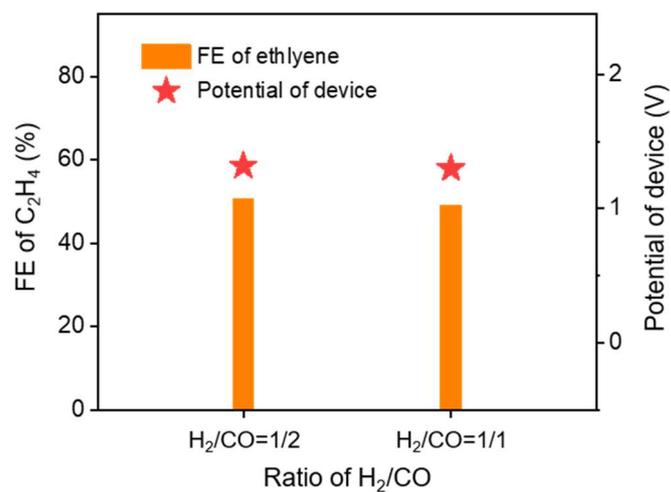
Fig. S17 The effect of different ratio of H_2 to CO on the performance of direct electrolysis of crude syngas containing 2% H_2S.

221 **Table S1.** The FE of CORR products at the cathode when dealing with 0% H_2S-
222 contained syngas with 1 M NaOH as electrolyte.

223

Current density (mA cm^{-2})	FE of products (%)				Selectivity of ethylene (%)
	C_2H_4	EtOH	AcO$^-$	n-PrOH	
5	41.6	7.9	2.0	14.4	63.1
10	50.2	8.9	1.1	8.2	73.4
15	39.0	6.0	1.9	5.9	73.9
20	25.9	6.8	0.8	3.7	69.6

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227 **Table S2.** The FE of CORR products at the cathode when dealing with 2% H_2S-
228 contained syngas with 1 M NaOH as electrolyte.

229

Current density (mA cm^{-2})	FE of products (%)				Selectivity of ethylene (%)
	C_2H_4	EtOH	AcO$^-$	n-PrOH	
5	41.1	3.7	1.7	13.4	68.6
10	50.6	6.8	1.1	7.0	77.3
15	37.8	8.2	2.1	6.2	69.6
20	25.4	6.7	1.0	6.6	64.0

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233

234 **Table S3.** The FE of CORR products at the cathode when dealing with 10% H_2S-
235 contained syngas with 1 M NaOH as electrolyte.

236

Current density (mA cm^{-2})	FE of products (%)				Selectivity of ethylene (%)
	C_2H_4	EtOH	AcO$^-$	n-PrOH	
5	40.6	10.0	2.8	12.2	61.9
10	49.7	8.4	1.0	7.2	75.0
15	38.5	7.7	0.9	6.6	71.7
20	25.7	6.1	1.1	4.2	69.3

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239 **References**

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241 1   M. Zhang, J. Guan, Y. Tu, S. Chen, Y. Wang, S. Wang, L. Yu, C. Ma, D. Deng and X. Bao,
242   *Energy Environ. Sci.*, 2020, **13**, 119-126.
243 2   R. Chen, H. Y. Su, D. Liu, R. Huang, X. Meng, X. Cui, Z. Q. Tian, D. H. Zhang and D. Deng,
244   *Angew. Chem. Int. Ed.*, 2020, **59**, 154-160.

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