Electronic Supplementary Information

Carbon nanofibers@NiSe core/sheath nanostructures as efficient electrocatalysts for integrating highly selective methanol conversion and less-energy intensive hydrogen production

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1 Method

1.1 Chemicals

Carbon nanofibers (D × L 100 nm × 20-200 μm), Nickel(II) acetylacetonate (Ni(acac)$_2$, 95%), diphenyl diselenide (DPDSe 98%), oleylamine (OLA, technical grade, 70%), Nafion solution (~5% in a mixture of lower aliphatic alcohols and water) were obtained from Sigma-Aldrich. IrO$_2$ (99.9% trace metals basis) and Pt/C (20wt%) were purchased from Alfa Aesar. KOH (GR), methanol (GR) and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were used as received without any further purification.

1.2 Synthesis

In a typical procedure, Ni(acac)$_2$ (256.9mg), CNFs (137.7mg) and 20 mL OLA were added to a 100 mL round-bottom *Schlenk* flask at room temperature. The stoichiometric mass ratio between the equivalent NiSe and CNFs is 1:1, controlled by the dosages of precursors. The flask was evacuated and then filled up by argon three times using the *Schlenk* line, and then the mixture under an argon atmosphere was heated to 80 °C for 30 mins for totally dissolving the Ni(acac)$_2$ in OLA. Then the sealed flask with mixture in it was treated via sonication at 60 °C for 4 hours in order to improve the dispersibility of CNFs in OLA.

At the same time, DPDSe (156.1mg) was mixed with 4 mL OLA in a vial, which was preheated to 80 °C on a hot plate. Consequently, the flask was heated to 215 °C under an argon atmosphere. When the temperature of the flask reaches 200 °C, the DPDSe solution was injected by syringe. After injection, the reaction was allowed to proceed for 8 min with continuous stirring. The reaction was terminated by taking the flask away from the heating oil bath and allowed to cool to room temperature naturally. The as-synthesized CNFs@NiSe sample was then washed using xylene and isopropanol twice each and separated by centrifugation. The sample was finally dispersed in isopropanol for further characterization.

The NiSe nanocrystals with the absence of CNFs were also synthesized in the same procedure for a performance comparison.

1.3 Catalyst characterization

The as-synthesized CNFs@NiSe core/sheath nanostructures were characterized using field emission scanning electron microscopy (FESEM, Hitachi SU-70 system) at accelerating voltages of 5-20 kV. Specifically, a small piece of silicon wafer was attached on the surface of SEM specimen stub by conductive copper tapes, and then one drop of the sample suspension was placed on the surface of silicon wafer and allowed to dry in air. The specimen was then conductively coated with platinum by a sputtering method to minimize charging effects under FESEM imaging conditions.

TEM analysis was conducted using a JEOL JEM-F200 field emission microscope equipped with a EMSIS Xarosa CCD camera and Oxford INCA (Aztec) EDS facility with the potential of performing transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) and EDS elemental analysis (line scan and mapping) of the CNFs@NiSe core/sheath nanostructures. To prepare the HRTEM specimens, one drop of the suspension was placed on a carbon film supported copper grid and allowed to dry in air before the specimens were transferred into the microscope.

Crystallographic and purity information on CNFs@NiSe core/sheath nanostructures were obtained using powder XRD. To analyze these materials, the as-synthesized samples (dispersed in isopropanol) after centrifugation and later air-dried upon deposition onto glass slides. Diffraction patterns of these materials were collected using a powder diffractometer (RIGAKU Smartlab) operating in the reflection mode with Cu K_{α} radiation in the 2θ range from 10º to 75º.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a

photoelectron spectrometer using Al Kα radiation as the excitation source (ESCALAB 250Xi). All the peaks were calibrated with C 1s spectrum at binding energy of 284.8 eV.

1.4 Preparation of Working Electrode

The catalyst (CNFs@NiSe) modified carbon cloth electrode acted as both cathode and anode electrode. Prior to the modification, carbon cloth (CC) was cut into 15 mm × 5 mm rectangular pieces, and then they were rinsed with water and ethanol thoroughly under sonication to remove residual organic species. For electrode modification, 5 mg dried catalyst (CNFs@NiSe) was dispersed in IPA (950 μL), and then 50 μL 5 wt % Nafion solution was added. The mixed solution was followed by ultrasonication for 30 min to obtain a homogeneous catalyst suspension. Then 25 μL catalyst ink was dropped on the carbon cloth (loading area 5 mm × 5 mm) yielding a mass loading of 0.5 mg cm^{-2}. The modified electrode (CNFs@NiSe/CC) was dried at ambient temperature before electrochemical measurements.

For the preparation of control group, the carbon cloth electrodes modified by CNFs mixed with NiSe (mass ratio 1:1), NiSe, CNFs and commercial IrO$_2$ were also prepared in the same procedure, denoted as CNFs/NiSe/CC, NiSe/CC, CNFs/CC and IrO$_2$/CC, respectively.

1.5 Electrocatalytic experiments

The electrochemical experiments were conducted in an H-type two-compartment cell in which the anode and cathode compartments were separated by an anion exchange membrane (AMI-7001, MI, USA). The catalyst modified electrodes were used for both cathode and anode reactions. The 1.0 M KOH containing 1.0 M methanol was used in the anode compartment, whereas 1.0 M KOH was used in the cathode compartment. The electrolyte volume is 70 mL for each compartment.

The electrochemical measurements were conducted on a CHI 760E electrochemical workstation (CH Instruments, Inc. Shanghai, China) at room temperature with standard three-electrode system. Linear Sweep Voltammetry (LSV) was measured at a scan rate of 5 mV s^{-1}.

All potentials were referenced to an Ag/AgCl (sat. KCl) reference electrode. All potentials were calibrated with respect to the reversible hydrogen electrode (RHE) through RHE calibration. $E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + E_{\text{RHE vs Ag/AgCl}}$. The potentials were corrected according to the formula: $E=E_{\text{applied}}-iR$, where i is the current flowing through the cell, and R is the ohmic resistance of the cell. The resistances (R) were measured by the iR compensation function available on the electrochemical workstation.

Electrochemical impedance spectroscopy (EIS) measurements were taken in frequency range of 0.01 Hz ~ 100 kHz at 0.6 V vs Ag/AgCl (sat. KCl) with an AC amplitude of 5 mV. The double-layer capacitance (C_{dl}) were obtained by collecting CV curves with scan rates of 20 to 120 mV s^{-1} with an interval of 20 mV s^{-1} in the potential range of 1.00 V to 1.10 V (vs RHE).

1.6 Methanol conversion and product quantification

The electrochemical oxidation of methanol was carried out at room temperature with stirring by chronoamperometry (*i-t*) at 0.6 V vs Ag/AgCl (sat. KCl) (= 1.62 V vs RHE) for 0-20 hours.

The identification of molecular structure of formate in the anode product is conducted by Nuclear magnetic resonance (NMR) spectroscopy were recorded on Bruker AVANCE Ⅲ 600MHZ instruments at 600 MHz (^{1}H NMR) and 150 MHz (^{13}C NMR). All the NMR spectra were measured in D$_2$O.

The identification and quantification of formate product are conducted by Ion Chromatography (IC) and determined by calibration curve. The anode solution was then proportionately (200 fold) diluted and analyzed by Ion Chromatography (IC) to detect the formate generation. The Ion Chromatography (IC) was carried out on a CIC-D120 ion chromatograph (Shenghan Chromatography Technology Co., Ltd, Qingdao, China) equipped with an SH-AC-3 column.

The identification and quantification of the formate products were determined by calibration curve by applying standard formate solutions with known concentrations of commercially purchased pure sodium formate (chromatographic pure).

The Faradaic efficiency (FE) of formate generation was calculated using the following equation:

$$FE(formate, \%) = \frac{mole\ of\ formed\ formate}{total\ charge\ passed\ /\ (4 \times F)} \times 100\%$$

$$FE(formate, \%) = \frac{4 \times 96485(\frac{C}{mol}) \times \omega_t(\frac{mg}{L}) \times V(L) \times 10^{-3}(\frac{g}{mg})}{M_{formate}(\frac{g}{mol}) \times \int_0^t I(A)dt} \times 100\%$$

where

F is the Faraday constant (96485 C mol^{-1}).

ω_t(mg L^{-1}) is the concentration of formed formate in the solution from the anode compartment of the cell, namely, the IC data (ppm $\times$ 10^{-6}). The unit of ppm here is mass(formate)/volume(solution).

V(L) is the total volume of the solution in the anode compartment of the cell.

$M_{formate}$(g mol^{-1}) is the molecular weight of formate (HCOO$^-$) equal to 45.02 g mol^{-1}.

I(A) is the current recorded by the electrochemical workstation in the chronoamperometry (i-t) mode.

The electrochemical oxidation of methanol was also carried out at room temperature with stirring by chronoamperometry (i-t) at 0.3, 0.4, 0.5, 0.7, 0.8 V, 0.9, and 1.0 V vs Ag/AgCl (sat. KCl) (=1.32, 1.42, 1.52, 1.72, 1.82, 1.92, and 2.02 V vs RHE) for 1 hour, respectively. The following measurements and analysis for formate production and Faradaic efficiency were same to the methods mentioned above.

1.7 Detection of gas products at the anode

The possible gas production (O_2, etc.) at the anode was tested by the gas chromatography (5977B MSD, Agilent Technologies) with a flame ionization detector (FID) and a thermal conductivity detector (TCD), when the electrochemical oxidation of methanol was carried out at room temperature with stirring by chronoamperometry (i-t) at 0.6 V vs Ag/AgCl (sat. KCl) (= 1.62 V vs RHE) in the anode compartment. Argon (purity: 99.999%) was used as a carrier gas with a constant flow rate of 20 cm^3 min^{-1}. Before the chronoamperometry experiment, the anode compartment was purged with Ar for 30 min, and then the first GC sampling was conducted in order to demonstrate the absolute absence of O_2 residuals in the anode compartment. Then the chronoamperometry was started and the GC sampling was conducted at the electrocatalytic reaction time of 30, 60 and 90 min. The results confirmed that oxygen (O_2) and other air products were not detected during the chronoamperometry experiment.

1.8 H_2 production at the cathode and product quantification

When the electrochemical oxidation of methanol was carried out at room temperature with stirring by chronoamperometry (i-t) at 0.6 V vs Ag/AgCl (sat. KCl) (= 1.62 V vs RHE) in the anode compartment, the H_2 production at the cathode (counter electrode) was detected in the meantime by the gas chromatography (GC9790plus, Fuli instruments) with a thermal conductivity detector (TCD). Argon (purity: 99.999%) was used as a carrier gas with a constant flow rate of 20 cm^3 min^{-1}. The GC sampling was conducted in every 10 minutes. A stable flow rate of mixed gas (the produced H_2 and the carrier gas) was achieved after 30 minutes' electrocatalytic reaction, which gave the accurate GC traces for H_2 production. At least three accurate trace curves were collected for further analysis (40, 50 and 60 min of the electrocatalytic reaction).

The identification and quantification of the H_2 products were determined by calibration curve by applying commercial standard H_2 gas with known concentrations.

The formation rate (mol s^{-1}) of H$_2$ was calculated using the following equation:

$$n_v(H_2, mol/s) = \frac{Vvp_0}{RT_0}$$

$$n_v(H_2, mol/s) = \frac{V(\frac{m^3}{s}) \times v(vol\ ratio) \times 1.01 \times 10^5(\frac{N}{m^2})}{8.314(\frac{N\ m}{mol\ K}) \times 298.15(K)}$$

The Faradaic efficiency (FE) of H$_2$ production was calculated using the following equation:

$$FE(H_2, \%) = \frac{mole\ of\ formed\ H_2}{total\ charge\ passed\ /\ (2 \times F)} \times 100\%$$

$$FE(H_2, \%) = \frac{2FVvp_0}{RT_0I} \times 100\%$$

$$FE(H_2, \%) = \frac{2 \times 96485(\frac{C}{mol}) \times V(\frac{m^3}{s}) \times v(vol\ ratio) \times 1.01 \times 10^5(\frac{N}{m^2})}{8.314(\frac{N\ m}{mol\ K}) \times 298.15(K) \times I(A)} \times 100\%$$

where

F is the Faraday constant (96485 C mol^{-1}).

v(vol ratio) is the volume concentration of H$_2$ in the exhaust gas from the cathode compartment of the cell, namely, the GC data (volume ppm $\times$ 10^{-6}). The unit of ppm here is volume(H$_2$)/volume(total).

V(m^3 s^{-1}) is the gas flow rate measured by a flow meter at room temperature and under ambient pressure.

I(A) is the current recorded by the electrochemical workstation in the chronoamperometry (*i-t*) mode.

1.9 Computational Details

The spin-polarized density functional theory (DFT) calculations were performed using

the Vienna *ab-initio* Simulation Package (VASP) [s1,s2]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional were used to describe the electronic exchange and correlation effects [s3]. The experimentally obtained lattice parameters were used for the DFT calculation, *i.e.* $a=b=3.66$Å, $c=5.33$Å, $\alpha=\beta=90°$, $\gamma=120°$ for NiSe system. To model the adsorption of intermediates on the NiSe (102) facets which were observed experimentally, a $p(2\times3)$ slab model along NiSe (102) facets was built with a vacuum of 15 Å was employed, which makes a supercell of $a=16.56$Å, $b=10.98$Å, $c=21.46$ Å, $\alpha=\beta=\gamma=90°$. The gamma point was used for geometric optimization with a cutoff energy of 500 eV. The criteria for the geometry optimization and ionic steps were set as 0.02 eV Å^{-1} and 10^{-5} eV for the force and energy, respectively. All the top, bridged and hollow sites are systematically considered for the adsorptions. Following Nørskov's strategy [s4], the adsorption energies ($\varDelta E$) of intermediates (OCH$_3$, OCH$_2$OH, HCOO) on the substrate were described as:

$$\varDelta E(OCH_3) = E(sub/OCH_3) - [E(sub) + E(CH_3OH) - E(H_2)/2]$$

$$\varDelta E(OCH_2OH) = E(sub/OCH_2OH) - [E(sub) + E(HOCH_2OH) - E(H_2)/2]$$

$$\varDelta E(HCOO) = E(sub/HCOO) - [E(sub) + E(HCOOH) - E(H_2)/2]$$

where $E(sub/OCH_3)$, $E(sub/OCH_2OH)$ and $E(sub/HCOO)$ are the total energies of OCH$_3$, OCH$_2$OH and HCOO groups on the substrate, respectively; $\varDelta E(sub)$, $E(CH_3OH)$, $E(HOCH_2OH)$, $E(HCOOH)$ and $E(H_2)$ denote the total energies of bare substrate, CH$_3$OH, HOCH$_2$OH, HCOOH and gas H$_2$, respectively.

The adsorption energies for CH$_3$OH, HCOOH and HCOOOH on the substrate were described as:

$$\varDelta E(CH_3OH) = E(sub/CH_3OH) - [E(sub) + E(CH_3OH)]$$

$$\varDelta E(HCOOH) = E(sub/HCOOH) - [E(sub) + E(HCOOH)]$$

$$\varDelta E(HCOOOH) = E(sub/HCOOOH) - [E(sub) + E(H_2CO_3)$$

Where $E(sub/CH_3OH)$, $E(HCOOH)$ and $E(sub/HCOOOH)$ are the total energies of CH$_3$OH, HCOOH and HCOOOH groups on the substrate, respectively; $E(sub)$, $E(CH_3OH)$, $E(HCOOH)$ and $E(sub/H_2CO_3)$ denote the total energies of the substrate, CH$_3$OH, HCOOH and H$_2$CO$_3$, respectively.

To account for the contribution from entropy, temperature and zero point energy, the Gibbs free energies of the intermediates was calculated at 298.15 K, and the Gibbs free energy change (ΔG) for the adsorption of intermediates H, OH, O, OOH and O$_2$ was calculated by

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

Where the E, ZPE, T, and S denote the calculated total energy, zero point energy, temperature, and entropy.

2 Tables

Table S1. Comparison of electrocatalytic methanol oxidation performance for the samples of CNFs@NiSe/CC, CNFs/NiSe/CC, NiSe/CC and IrO$_2$/CC at the anode in 1.0 M KOH containing 1.0 M methanol.

Catalysts[a]	Onset potential (V) at 1mA cm^{-2}	Potential (V) at 100 mA cm^{-2}	Potential (V) at 200 mA cm^{-2}	Potential (V) at 300 mA cm^{-2}	Potential (V) at 400 mA cm^{-2}	Tafel slope (mV dec^{-1})
CNFs@NiSe/CC	1.35	1.43	1.47	1.50	1.55	24
CNFs/NiSe/CC	1.38	1.52	1.62	1.70	1.79	40
NiSe/CC	1.39	1.59	1.75	1.91	2.06	77
IrO$_2$/CC	1.42	1.71	1.85	1.98	2.09	89

(a) All the parameters were measured under the same conditions.

Table S2. Comparison of the Tafel slopes of CNFs@NiSe/CC and the reported catalysts applied for the electrocatalytic oxidation or OER approaches.

Catalysts	Tafel slope (mV dec^{-1})	Organic candidates applied at the anode for electrocatalytic oxidation	The basic electrolyte at the anode	Ref. No. in the paper
Ni_3S_2/Nickel foam	136	5‑Hydroxymethylfurfural	1 M KOH	8
$CoSe_2$	84	hydrazine	1 M KOH	9
Nitrogen-doped carbon (NC)@$CuCo_2N_x$/carbon fiber	81	benzyl alcohol	1 M KOH	17
NiFe layered double hydroxide (LDH)	75	5-hydroxymethylfurfural	1 M KOH	14
$NiSe$/Ni_3Se_2/Nickel foam	69.2	OER	1 M KOH	4
NiSe/Nickel foam	64	OER	1 M KOH	31
$NiSe_2$/Nickel foam	63.1	OER	1 M KOH	27
Ni_2P/Nickel foam	55	hydrazine	1 M KOH	11
CoCu bi-metal-organic framework nanosheets	46.25	methanol	1 M KOH	10
Oxygen vacancy-rich $NiMoO_4$/Nickel foam	32.5	urea	1 M KOH	12
CNFs@NiSe/CC	**24**	**methanol**	**1 M KOH**	**In this work**

Table S3. The results and error values of generated formate concentration with CNFs@NiSe/CC anode. The chronoamperometry (*i-t*) was conducted at 1.62 V vs RHE (0.60 V vs Ag/AgCl) over time starting with 1.0 M KOH containing 1.0 M methanol. The data was calculated from the Ion Chromatography traces.

Reaction time	Generated formate concentration (mmol L^{-1})[a]			Statistical results (mean value ± error value, mmol L^{-1})	The calculated faradaic efficiency (%)
1 h	9.29	9.32	9.24	9.28 ± 0.04	99.94 ± 0.43
2 h	18.84	18.86	18.79	18.83 ± 0.03	98.82 ± 0.16
3 h	28.49	28.33	28.57	28.46 ± 0.10	98.62 ± 0.35
4 h	37.92	37.69	38.11	37.90 ± 0.17	98.36 ± 0.44
5 h	47.11	47.32	46.81	47.08 ± 0.21	97.85 ± 0.44
10 h	91.88	92.32	92.62	92.27 ± 0.30	96.88 ± 0.31
20 h	179.00	179.75	180.58	179.78 ± 0.65	97.90 ± 0.35

(a) Ion Chromatography measurements for each samples were repeated three times.

Table S4. The results and error values of generated formate concentration with CNFs@NiSe/CC anode. The chronoamperometry (*i-t*) was conducted at 1.32-2.02 V vs RHE (0.3-1.0 V vs Ag/AgCl) for 1 hour starting with 1.0 M KOH containing 1.0 M methanol. The data was calculated from the Ion Chromatography traces.

Potentials (V vs RHE)	Generated formate concentration (mmol L^{-1})[a]			Statistical results (mean value ± error value, mmol L^{-1})	The calculated faradaic efficiency (%)
1.32	0			0	/
1.42	1.16	1.15	1.17	1.16 ± 0.01	100.3 ± 0.86
1.52	4.21	4.22	4.18	4.20 ± 0.02	99.98 ± 0.48
1.62	9.29	9.32	9.24	9.28 ± 0.04	99.94 ± 0.43
1.72	12.05	12.14	12.19	12.13 ± 0.07	96.72 ± 0.56
1.82	14.59	14.47	14.36	14.47 ± 0.12	93.33 ± 0.77
1.92	16.09	16.21	16.30	16.20 ± 0.11	89.19 ± 0.61
2.02	17.09	17.27	17.43	17.27 ± 0.17	83.74 ± 0.82

(a) Ion Chromatography measurements for each samples were repeated three times.

Table S5. The results and error values of H_2 generation from the cathode compartment. The chronoamperometry (*i-t*) was conducted at 0.6 V vs Ag/AgCl (sat. KCl) (= 1.62 V vs RHE) with or without adding 1.0 M methanol in the anode compartment, and the data was calculated from the Gas Chromatography traces.

Electrolyte in the anode compartment	Generation rate of H_2 (10^{-8}mol s^{-1})[a][b]			Statistical results (mean value ± error value, 10^{-8} mol s^{-1})	The calculated faradaic efficiency (%)
1.0 M KOH + 1.0 M MtOH	35.73	35.08	36.19	35.67 ± 0.45	98.17 ± 1.91
1.0 M KOH	4.74	4.81	4.77	4.77 ± 0.03	92.08 ± 0.80

(a) GC sampling was conducted at 40, 50 and 60 min of the electrocatalytic reaction.

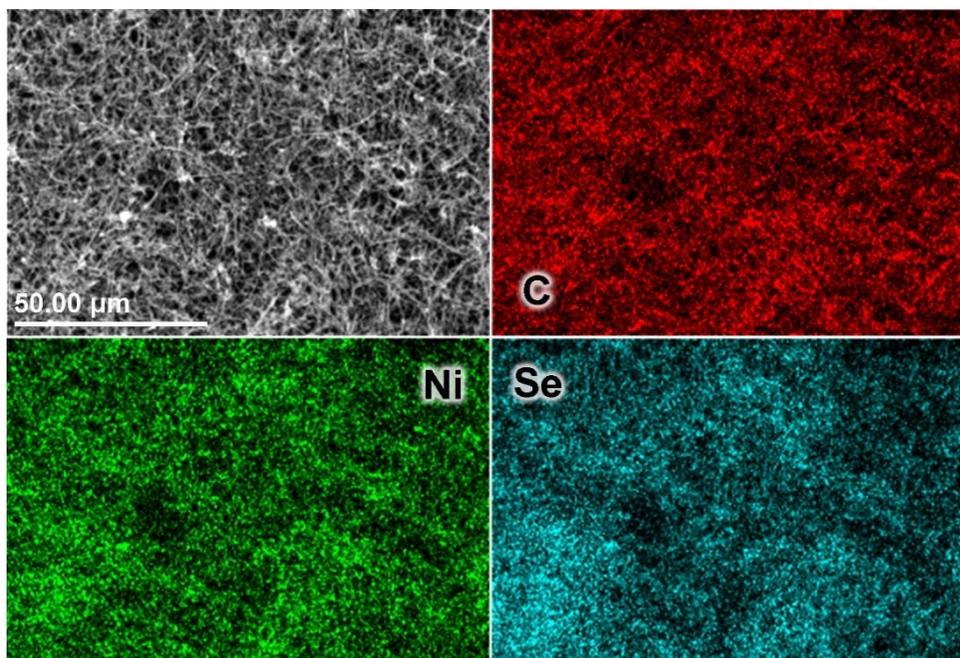(b) H_2 was generated from the cathode compartment in 1.0 M KOH.

3 Figures

Fig. S1 FESEM image and the corresponding EDS mapping of the as-synthesized CNFs@NiSe core/sheath nanostructures.
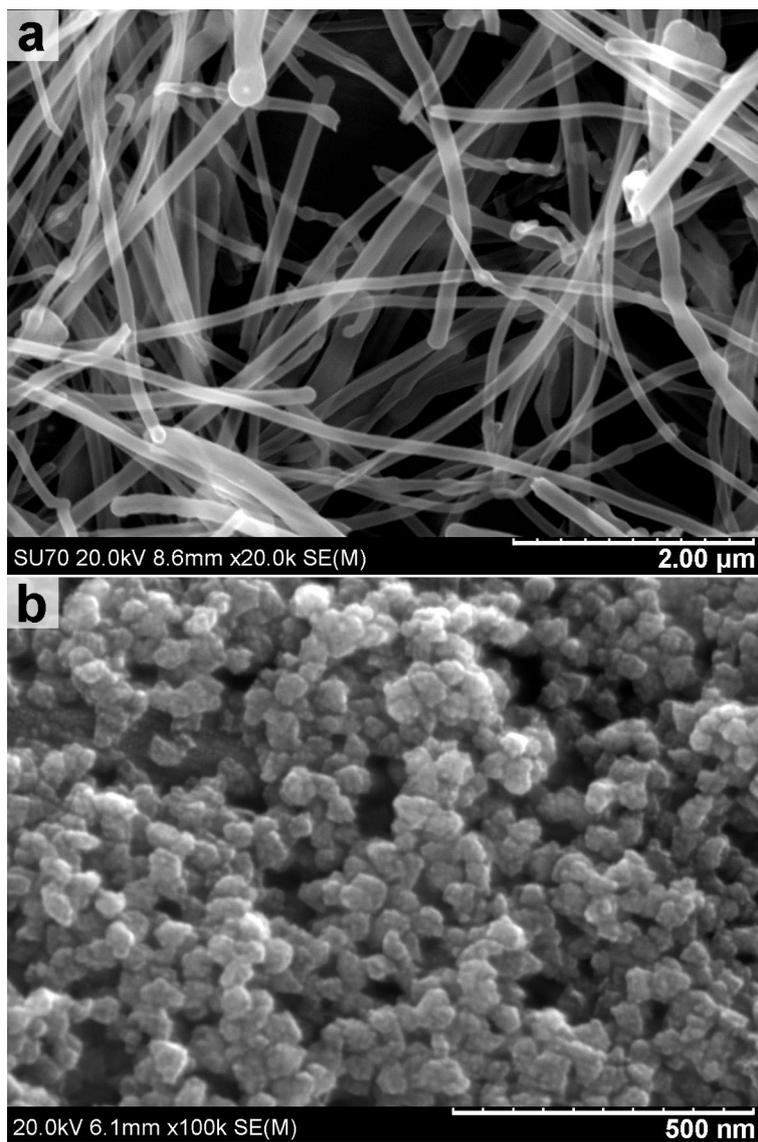
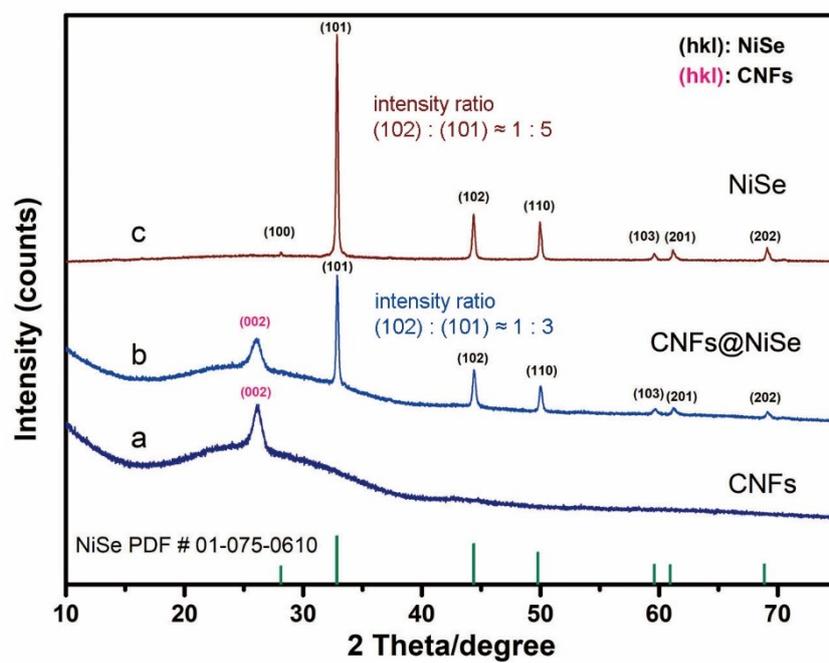**Fig. S2** FESEM images of (a) CNFs and (b) the as-synthesized NiSe nanocrystals.

Fig. S3 XRD patterns of (a) CNFs, (b) the as-synthesized CNFs@NiSe core/sheath nanostructures, and (c) NiSe nanocrystals.
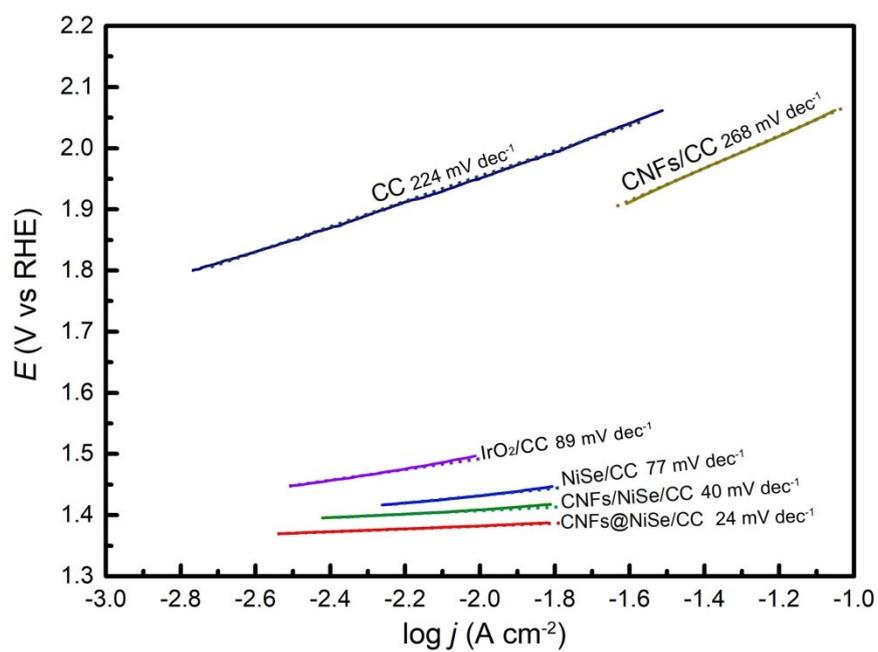
Fig. S4 The Tafel plots of CNFs@NiSe/CC, CNFs/NiSe/CC, NiSe/CC, IrO$_2$/CC, CNFs/CC and pristine carbon cloth.
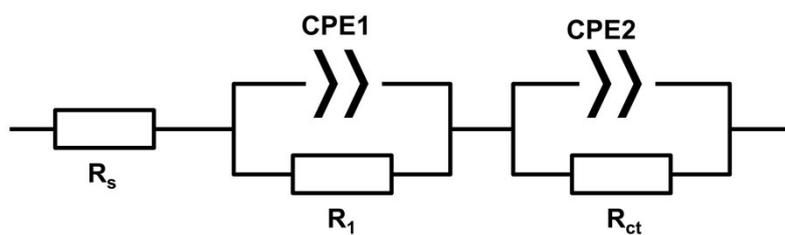
Fig. S5 The equivalent circuit model used to fit the Nyquist plots of EIS measurements.

The equivalent circuit is composed of a resistor (R_s) and two parallel combinations including a resistor (R_1, charge-transfer resistance (R_{ct})) and a constant phase element (CPE1, CPE2). R_s and R_{ct} are relevant to the electrocatalytic kinetics.

R_s represents the Ohmic resistance deriving from the electrolyte as well as all contacts.

R_{ct} reflects the charge transfer resistance at the interface between the catalyst and the electrolyte.

A small R_{ct} is favorable to fast charge transfer kinetics.
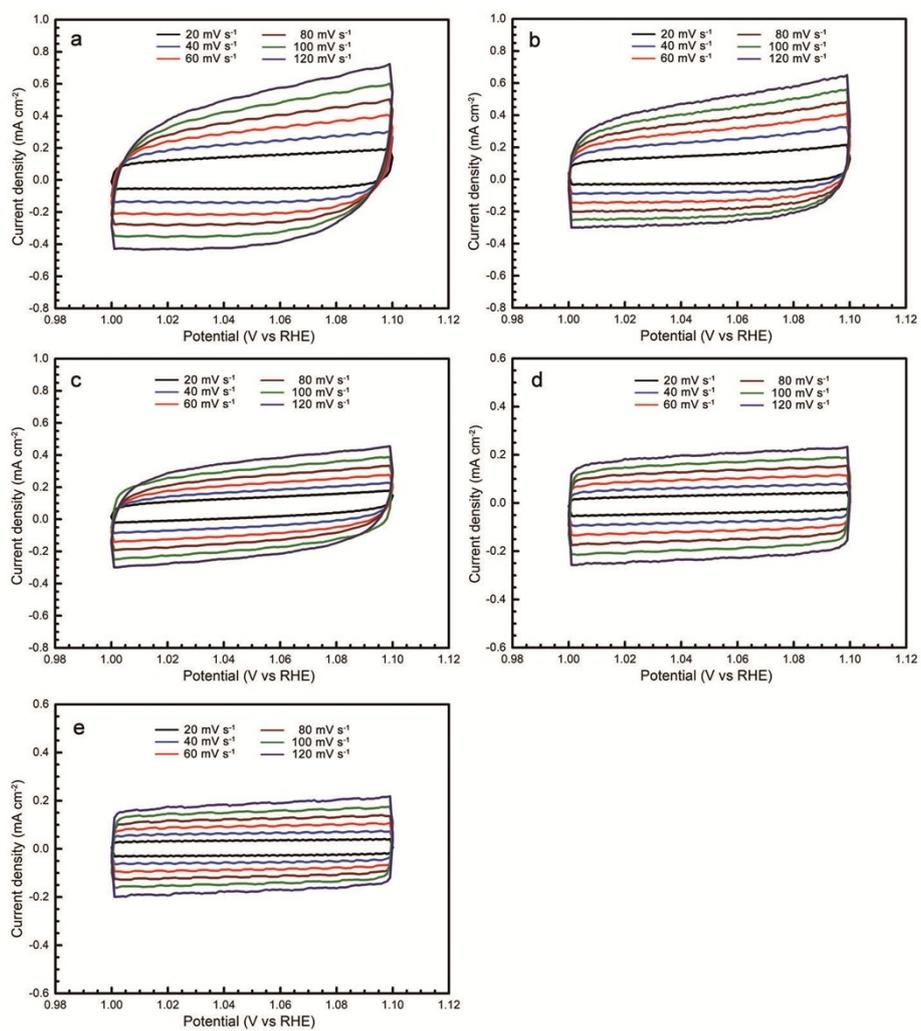
Fig. S6 Cyclic voltammetry curves of (a) CNFs@NiSe/CC, (b) CNFs/NiSe/CC, (c) NiSe/CC, (d) CNFs/CC and (e) pristine carbon cloth at different scan rates from 20 to 120 mV s⁻¹ in 1.0 M KOH containing 1.0 M methanol
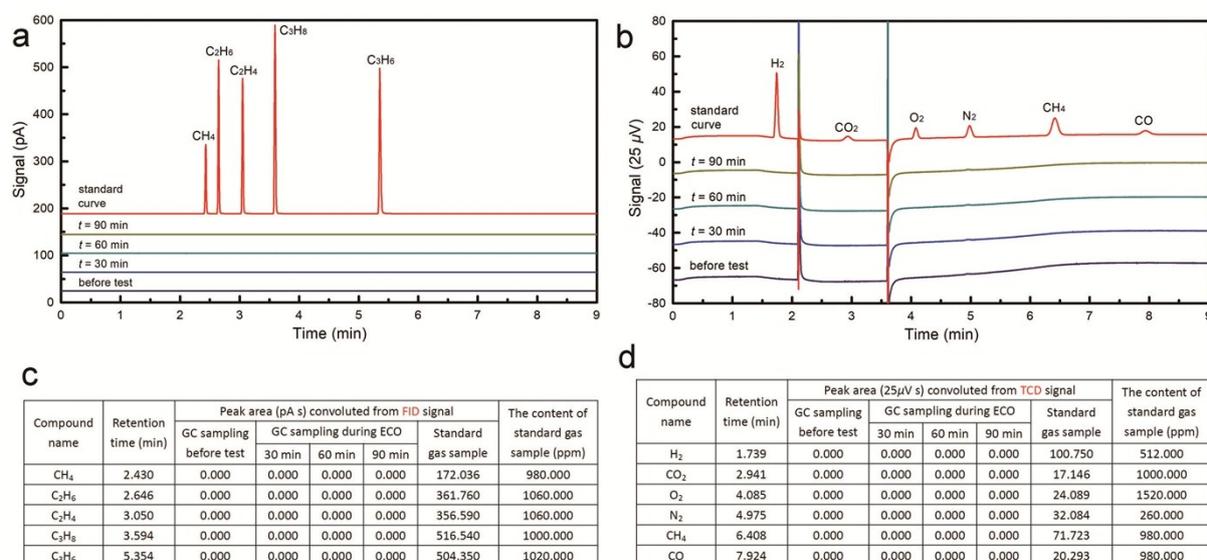
a

b

c

| Compound name | Retention time (min) | Peak area (pA s) convoluted from FID signal | | | | | The content of standard gas sample (ppm) |
| | | GC sampling before test | GC sampling during ECO | | | Standard gas sample | |
			30 min	60 min	90 min		
CH$_4$	2.430	0.000	0.000	0.000	0.000	172.036	980.000
C$_2$H$_6$	2.646	0.000	0.000	0.000	0.000	361.760	1060.000
C$_2$H$_4$	3.050	0.000	0.000	0.000	0.000	356.590	1060.000
C$_3$H$_8$	3.594	0.000	0.000	0.000	0.000	516.540	1000.000
C$_3$H$_6$	5.354	0.000	0.000	0.000	0.000	504.350	1020.000

d

| Compound name | Retention time (min) | Peak area (25µV s) convoluted from TCD signal | | | | | The content of standard gas sample (ppm) |
| | | GC sampling before test | GC sampling during ECO | | | Standard gas sample | |
			30 min	60 min	90 min		
H$_2$	1.739	0.000	0.000	0.000	0.000	100.750	512.000
CO$_2$	2.941	0.000	0.000	0.000	0.000	17.146	1000.000
O$_2$	4.085	0.000	0.000	0.000	0.000	24.089	1520.000
N$_2$	4.975	0.000	0.000	0.000	0.000	32.084	260.000
CH$_4$	6.408	0.000	0.000	0.000	0.000	71.723	980.000
CO	7.924	0.000	0.000	0.000	0.000	20.293	980.000

Fig. S7 Gas chromatography (GC) traces detected from the anode. (a & b) Gas chromatography (GC) traces detected from the anode before and during the chronoamperometry (*i-t*) experiment (ECO reaction) at 0.6 V vs Ag/AgCl (sat. KCl) (= 1.62 V vs RHE) in the anode compartment; (c & d) the tables of correponding quantified results based on the standard curves of gas compounds. The calibriated standard GC values of gas compounds are also included in the figure and table.
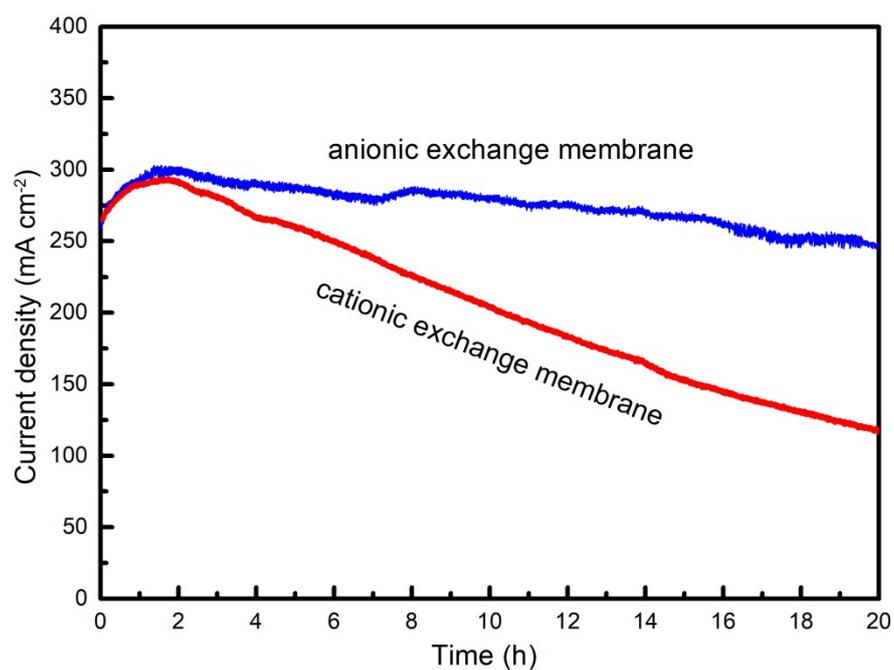
Fig. S8 Chronoamperometry (*i-t*) curves of CNFs@NiSe /CC using different exchange membranes. *i-t* curves at a specified voltage of 1.62 V (vs RHE) for formate generation in an H-type two-compartment cell in which the anode and cathode compartments were separated by the anionic (AMI-7001, USA) or cationic (CMI-7000, USA) exchange membranes.
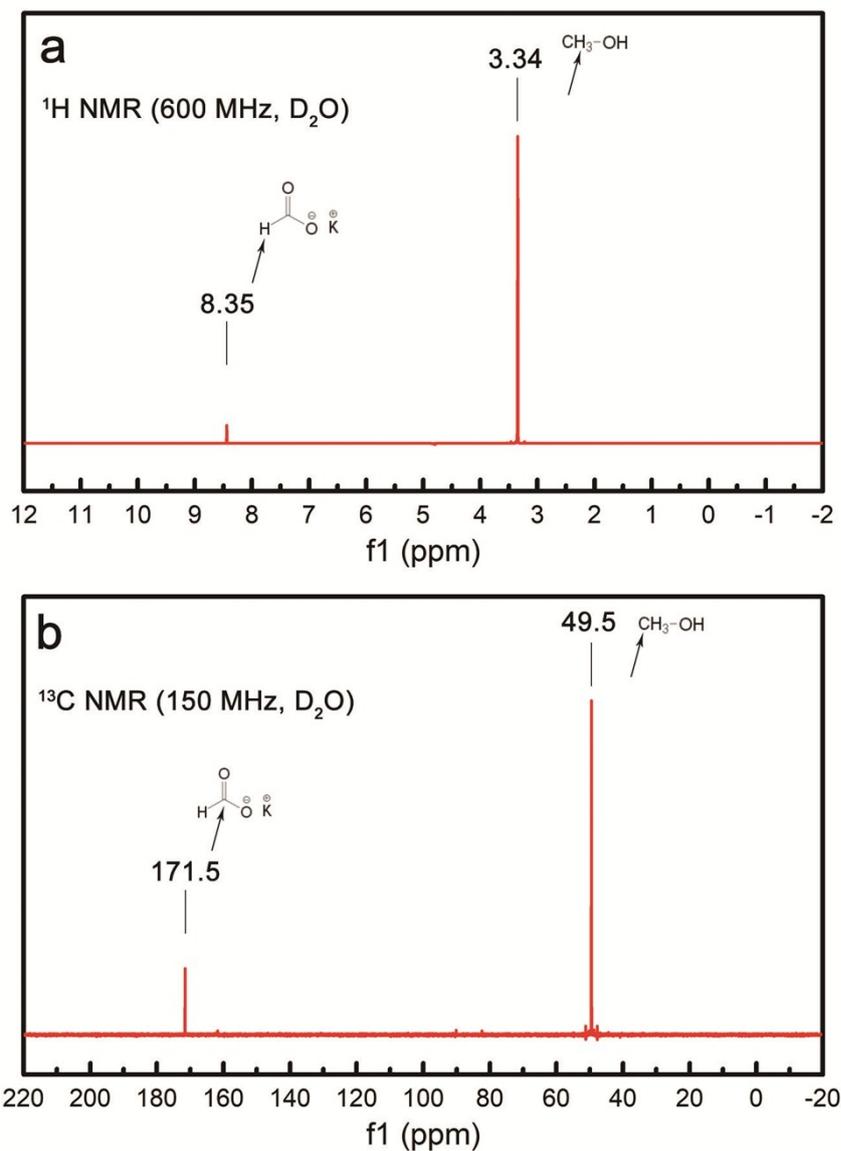
Fig. S9 The (a) ^{1}H and (b) ^{13}C NMR spectra of the anode product obtained through the electrochemical methanol oxidation by chronoamperometry (*i-t*) at 1.62 V vs RHE for 20 hours starting in 1.0 M KOH containing 1.0 M methanol.
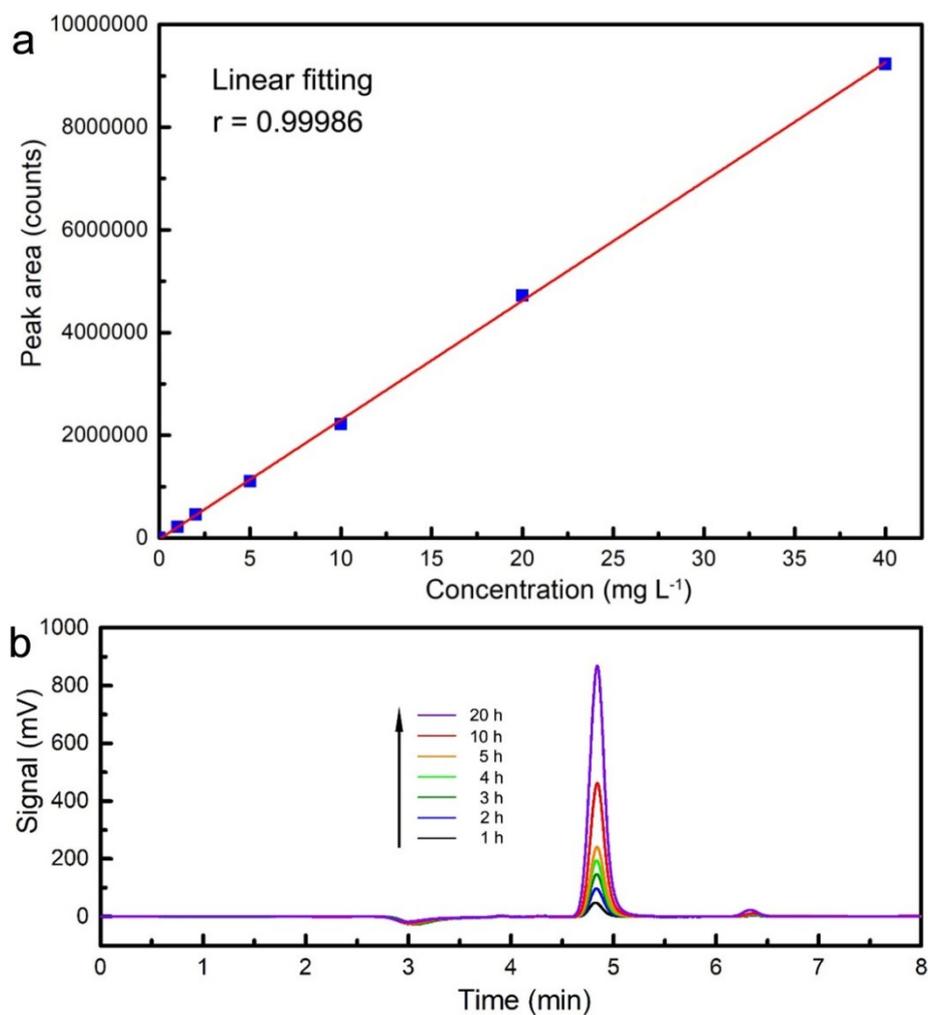
Fig. S10 The standard calibration curve of formate and experimental IC chromatogram traces. (a) The establishment of formate calibration curve by linear fitting based on the IC chromatogram traces. (b) The detection of formate generation from methanol electrooxidation using a CNFs@NiSe/CC electrode at a specified voltage of 1.62 V (vs RHE) for 20 hours.

The identification and quantification of the formate products were determined by calibration curve by applying standard formate solutions with known concentrations of commercially purchased pure sodium formate (chromatographic pure).

A mixture of 2.4 mM Na_2CO_3 and 6 mM $NaHCO_3$ is used as the mobile phase solution, and the flow rate is 1.0 mL min^{-1}. IC sampling for every experiment was repeated at least three times, and the median data was employed for plotting the curves.
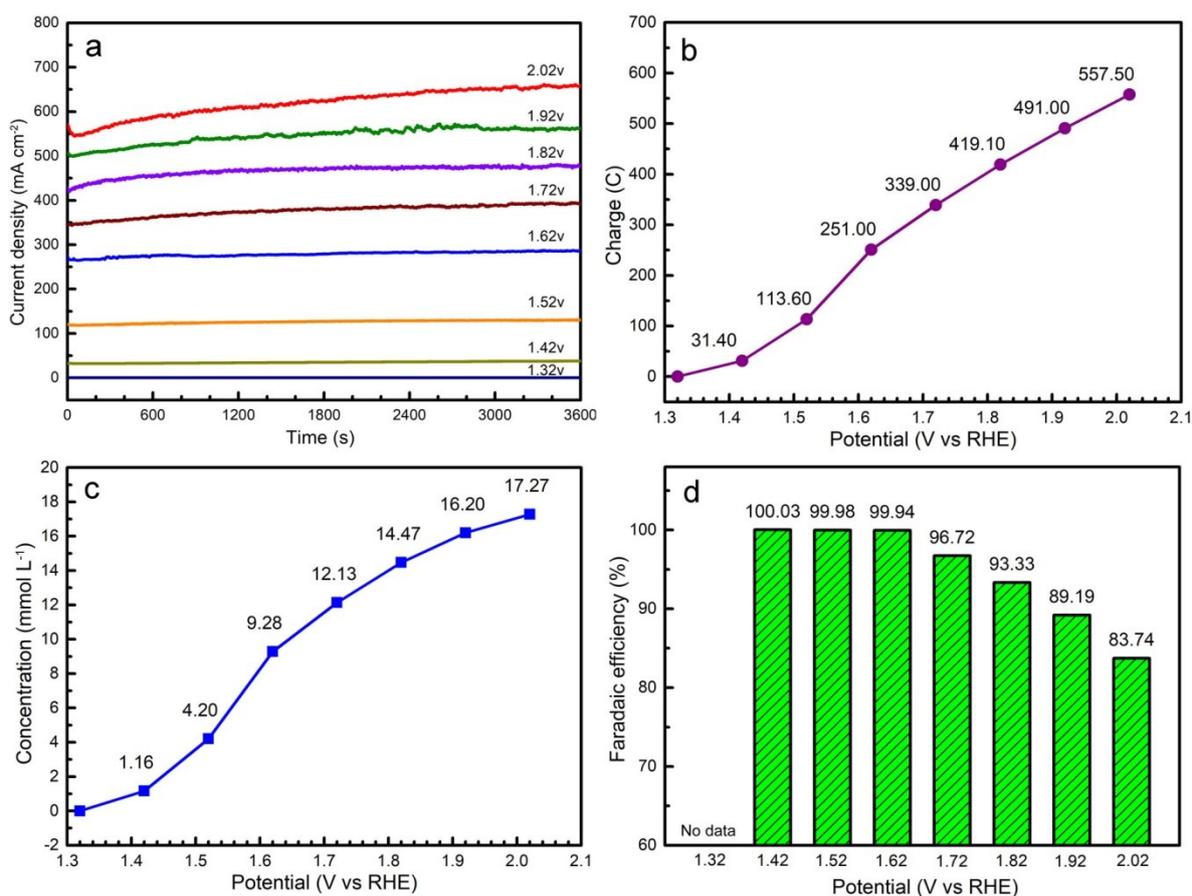
Fig. S11 Selective electrocatalytic methanol conversion to formate with CNFs@NiSe electrocatalysts at different potentials. (a) Chronoamperometry (*i-t*) curve of CNFs@NiSe/CC at 0.3–1.0 V vs Ag/AgCl (sat. KCl) (=1.32–2.02 V vs RHE) for 1 hour; (b) The passed electric charges; (c) The generated formate concentration with CNFs@NiSe/CC anode at different potentials; (d) The corresponding faradaic efficiencies for formate generation.
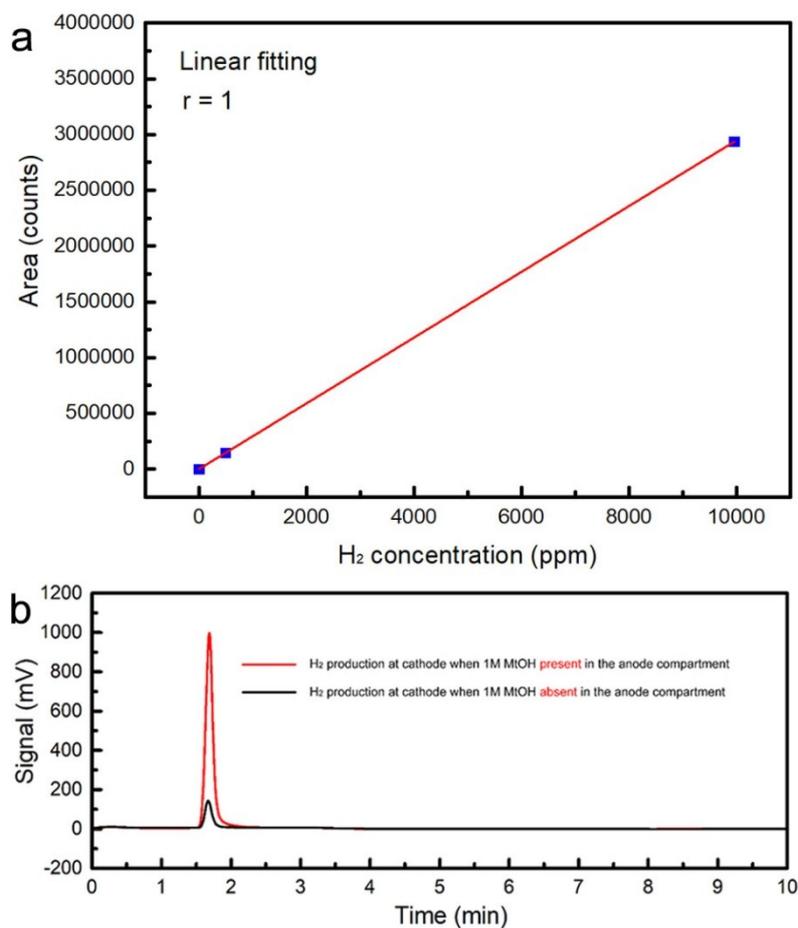
Fig. S12 H_2 calibration curve and the experimental gas chromatography (GC) traces. (a) The establishment of H_2 calibration curve by linear fitting based on the Gas chromatography. (b) The representative GC traces for detecting the H_2 generation from cathode electrode (counter electrode) using a CNFs@NiSe/CC electrode, when 1.0 M MtOH was present/absent in the anode compartment.

The other identical CNFs@NiSe/CC electrode was also used as the working electrode in the anode compartment, accompanied with the Ag/AgCl (Sat. KCl) reference electrode together. The cell was conducted at a specified voltage of 1.62 V (vs RHE). Argon (purity: 99.999%) was used as a carrier gas with a constant flow rate of 20 sccm (standard cubic centimeter per minute). GC sampling was conducted at 40, 50, and 60 minutes of the electrocatalytic reaction respectively, and the median data was employed for plotting the curves.

4 References

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