Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Ni Nanoparticles Decorated-MnO_2 Nanodendrites as High Selective and Efficient Catalysts for CO_2 Electroreduction

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Experimental Section

Synthesis of Ni NPs/MnO_2 NDs-CFs: In a typical procedure for synthesizing Ni NPs/MnO_2 NDs-CFs, the electrodeposition method was used, and all the experiments were carried out in a simple two-electrode cell by galvanostatic electrolysis. The graphite electrode was used as a counter electrode (spectral grade, 1.8 cm^2), and the carbon fibers (CFs) (Phychemi Company, Hong Kong) were utilized as a working electrode (0.5 cm×2 cm). Anodic electrodeposition was performed at a constant current of 0.20 mA/cm^2 in the solution of 0.01 M $Mn(CH_3COO)_2$ + 0.05 M CH_3COONH_4 at 70°C for 90 min. Ni nanoparticles were electrodeposited on MnO_2 NDs-CFs in solution of 0.01 M $NiSO_4$+0.02 M sodium citrate at 1.0 mA/cm^2 for 6 min at 30 °C.

Synthesis of MnO_2 NDs-CFs: In a typical procedure, the anodic electrodeposition was performed at a constant current of 0.2 mA/cm^2 in solution of 10 mL 0.01 M $Mn(CH_3COO)_2$ + 0.05 M CH_3COONH_4 at 70 °C for 90 min.

Synthesis of Ni NPs-CFs: In a typical procedure, Ni NPs were deposited on the surface of CFs to form Ni NPs-CFs by electrodeposition in solution of 15 mL 0.01 M $NiSO_4$ and 0.02 M sodium citrate at 1.0 mA/cm^2 for 6 min at 30 °C.

Characterizations: The purity and crystallinity of as-obtained samples were characterized by powder X-ray diffraction (XRD) on a Philips X'Pert Pro Super diffractometer using Cu K_α radiation (λ = 1.54178 Å). X-ray photoelectron spectra (XPS) were achieved on an ESCALAB MKII with Mg Kα ($h\upsilon$ = 1253.6 eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.8 eV. Field emission scanning electron microscopy (FE-SEM) images were performed by using a FEI Sirion-200 SEM. Transmission electron microscopy (TEM) images and high-resolution TEM image were acquired by using a JEOL-2010 TEM with an acceleration voltage of 200 kV. The liquid products were quantified by ^{1}H NMR (Bruker AVANCE AV III 400) spectroscopy, in which 0.5 mL electrolyte was mixed with 0.1 mL D_2O (deuterated water) and 0.05 μL dimethyl sulfoxide (DMSO, Sigma, 99.99%) was added as an internal standard. $HCOO^-$ content in the electrolyte is determined by liquid chromatography mass spectrometer (Shimadzu, analysis software: LCMS Solution 3.10). The samples were also characterized by Brunauer-Emmett-Teller (BET) oxygen and nitrogen sorption surface area measurements (Micromeritics ASAP 2010). The specific surface areas of the synthesized materials were calculated by the Brunauer-Emmett-Teller (BET) method.

All the electrochemical measurements were implemented in a three-electrode system at an electrochemical station (CHI 760D). The working electrode was Ni NPs/MnO_2 NDs-CFs. The graphite rod and the saturated calomel electrode (SCE) reference electrode served as the counter and reference electrodes, respectively. For CO_2 reduction experiments, linear sweep voltammetry with a scan rate of 5 mV/s was carried out in CO_2-saturated 0.1 M $KHCO_3$ solution (60 mL) (The $KHCO_3$ electrolyte was purged with CO_2 for 30 min prior to the measurement). The potential, measured against a SCE electrode, was converted to the potential versus reversible hydrogen electrode (RHE) according to E (RHE) = E (SCE) + E_0 (SCE) + 0.059 pH.

TOF values were calculated using Equation (1).[4-6]

$$TOF(s^{-1}) = (j \times A)/(2 \times F \times n) \quad (1)$$

Here, j (mA cm_{geo}^{-2}) is the measured current density at a definite overpotential, A (cm_{geo}^{-2}) is the surface area of the electrocatalysts, the number 2 means 2 electrons to reduce one mole of CO_2, F is Faraday's constant (96485.3 C/mol), and n is the moles of electrochemical materials on the electrode calculated from m and the molecular weight of the coated catalysts.

To acquire the ECSA of the working electrodes, their roughness factor (R_f) should be obtained firstly according to the equation: ECSA=$R_f S$, where S was generally equal to the geometric area of glassy carbon electrode (In this work, S=1.13 cm^{-2}). The R_f was determined by the relation $R_f = C_{dl}/60$ μF cm^{-2} based on the double-layer capacitance (C_{dl}) of a smooth oxide surface (60 μF cm^{-2}).[7] where the C_{dl} could be acquired by cyclic voltammetry measurement under the potential windows of -0.3~-0.2 V *vs.* SCE (0.1 M $KHCO_3$ solution). The scan rates were 2 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s and 100 mV/s. The C_{dl} was estimated by plotting the $j_a - j_c$ at -0.25 V (where j_c and j_a are the cathodic and anodic current densities, respectively) versus SCE against the scan rate, in which the slope was twice that of C_{dl}.

The Faradaic efficiency of formate was estimated from the ratio of the total amount of charge Q(C) passed through the sample and the total amount of formate produced n formate (mol). $Q=I \times t$, where I(A) refers to the reduction current at a specific applied potential, t is the time (s) for the constant reduction current. Assuming that two electrons are needed to produce one formate, the Faradaic efficiency can be calculated as follows: Faradaic efficiency/%=$2F \times n_{formate}/Q = 2F \times n_{formate}/(I \times t)$, where F is the Faraday constant, 96480 C/mol.

Calculation details: All the calculations were performed based on spin-polarized periodic density

functional theory (DFT) implemented in Gaussian 09 W.[1] The electronion interactions were described by the projector augmented wave (PAW) method and the electron exchange and correlation energy were treated with the gradient corrected Perdew-Burke-Ernzerh (GGA-PBE) functional.[2] The kinetic cutoff energy for plane-wave basis set was set to be 400 eV. The total energy convergence was set to be lower than 10^{-5} eV, and the force convergence was set to be smaller than 0.02 eV/Å. The dipole corrections were also used to the slab exposed (110) surface.

References

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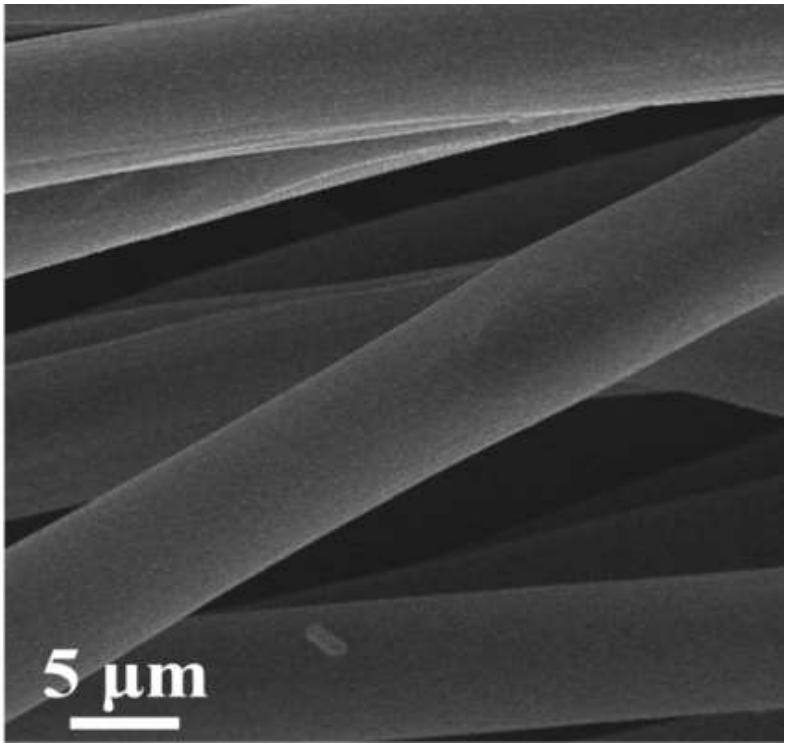

Figure S1 SEM image of pristine CFs.

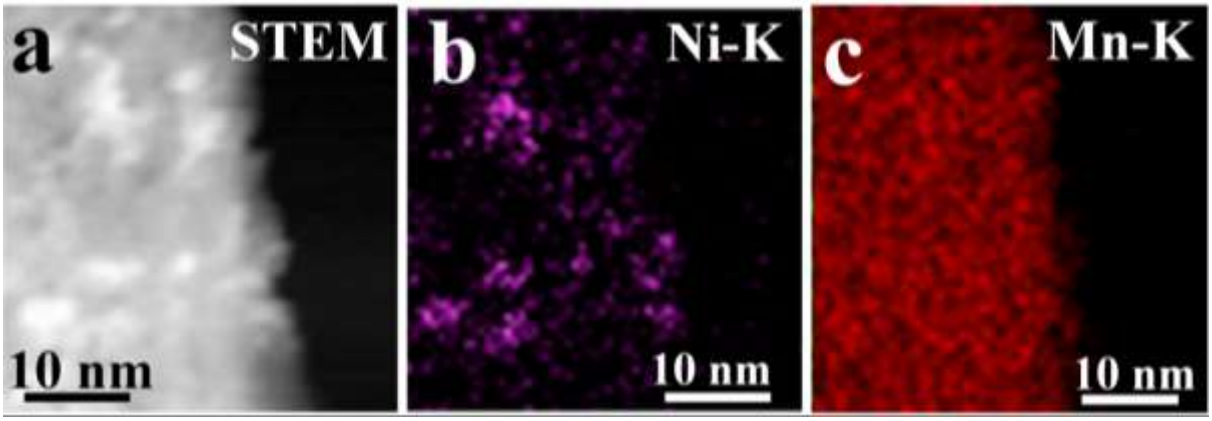

Figure S2. STEM-EDS mapping images of (a) STEM image of a part of Ni NPs/MnO_2 NDs, (b) EDS elemental mapping of Ni-K, and (c) Mn-K.

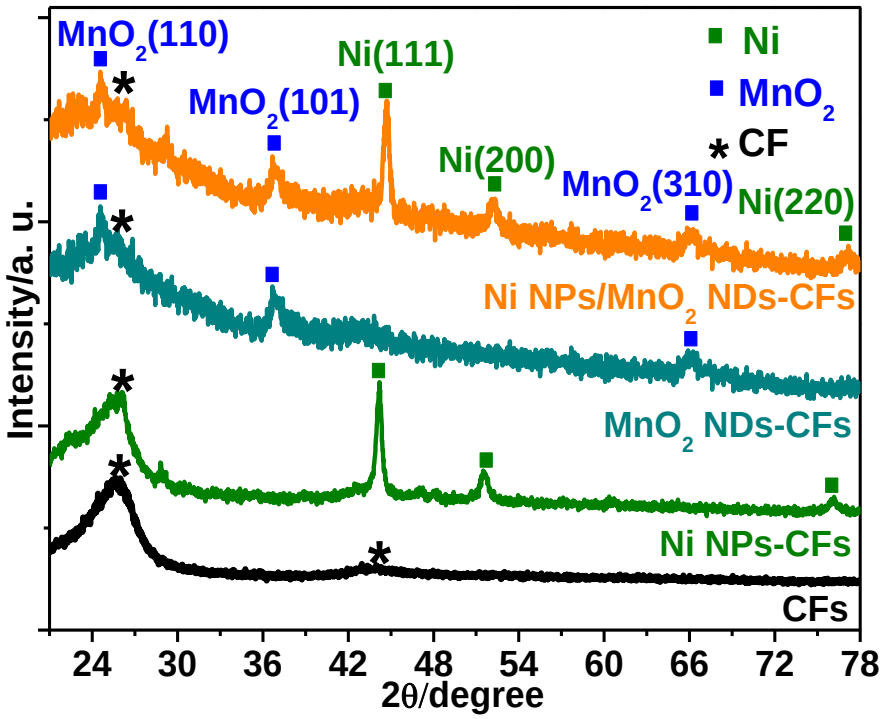

Figure S3. XRD patterns of the CF, Ni NPs-CF, MnO_2 NDs-CFs and Ni NPs/MnO_2 NDs-CFs.

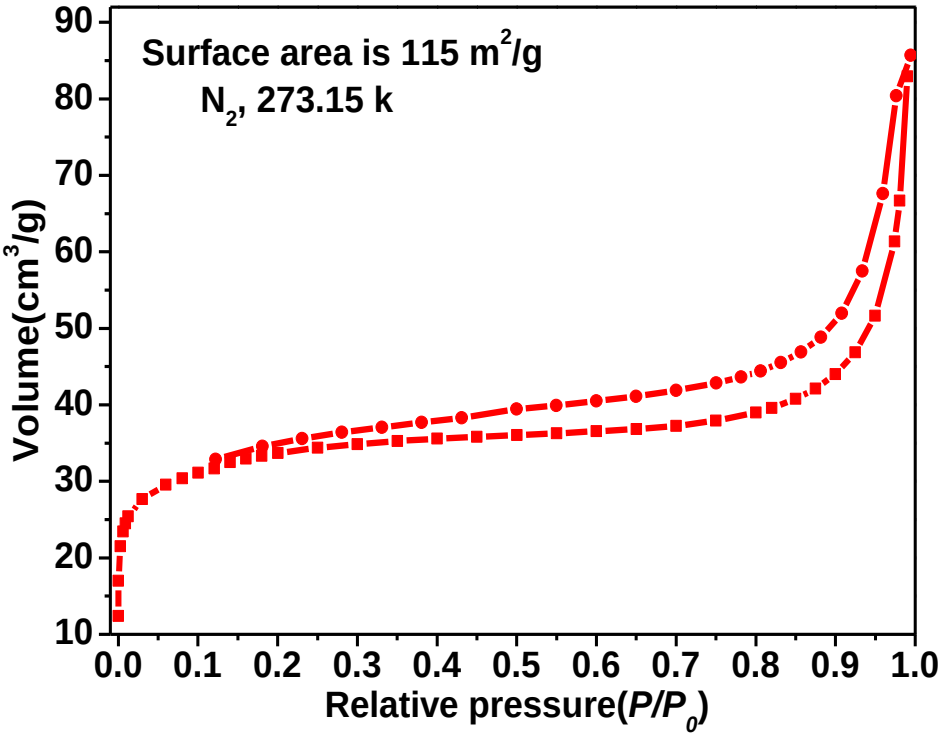

Figure S4. BET curve and surface area of Ni NPs/MnO_2 NDs.

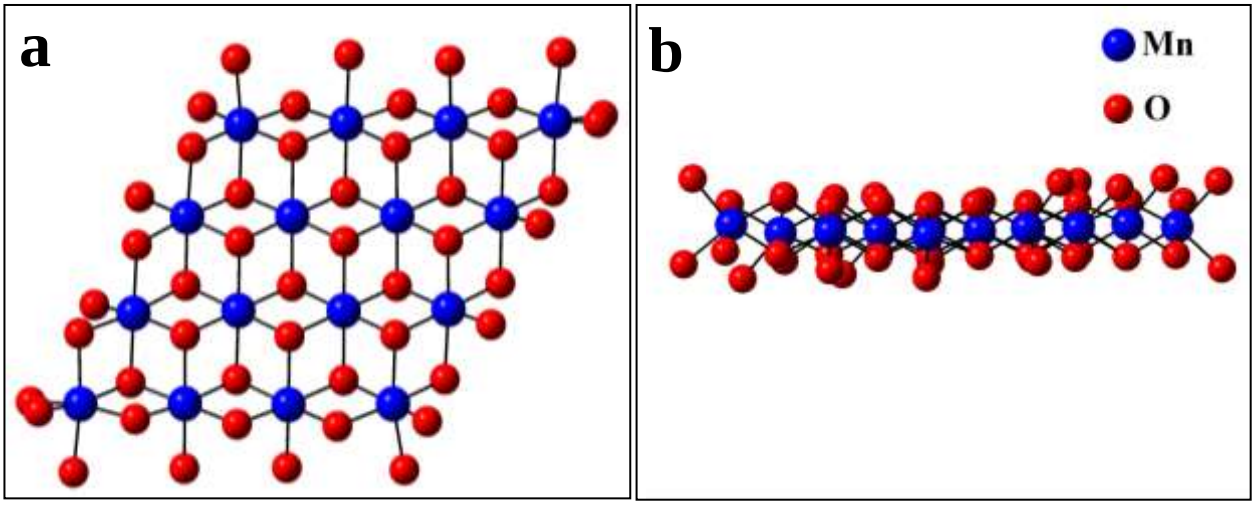

Figure S5. The optimized simplified structure of MnO_2 cluster. (a) Top view; (b) side view.

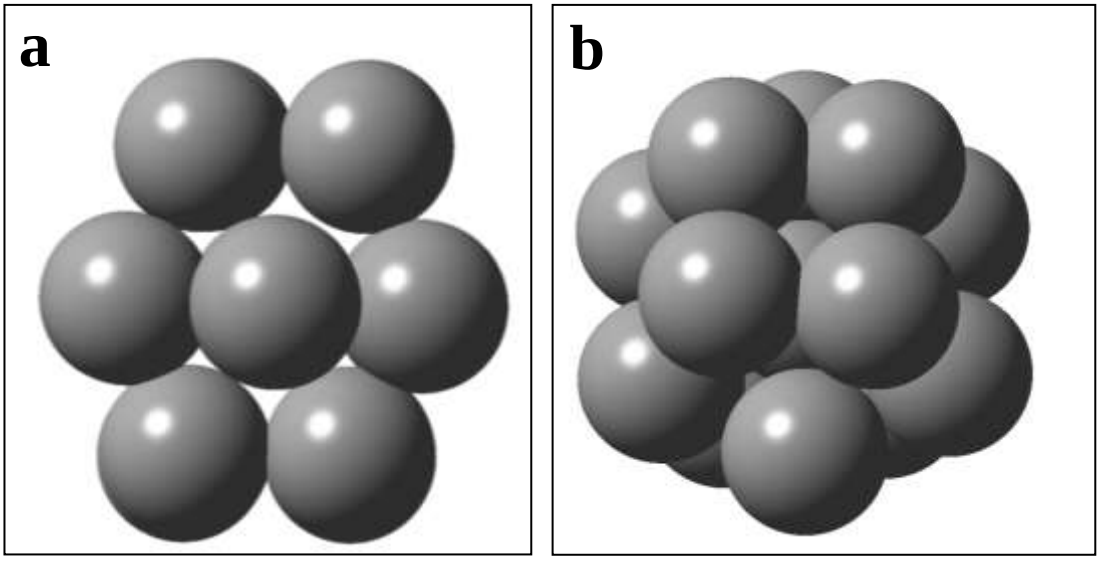

Figure S6. The optimized simplified structure of Ni cluster (a) Top view; (b) side view.

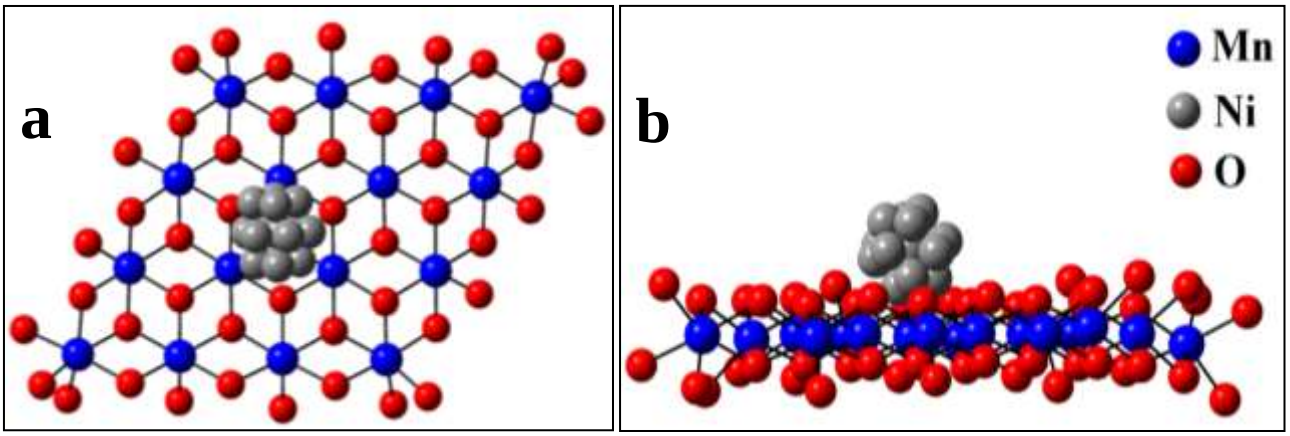

Figure S7. Optimized simplified structure of MnO_2/Ni cluster (a) Top view; (b) side view.

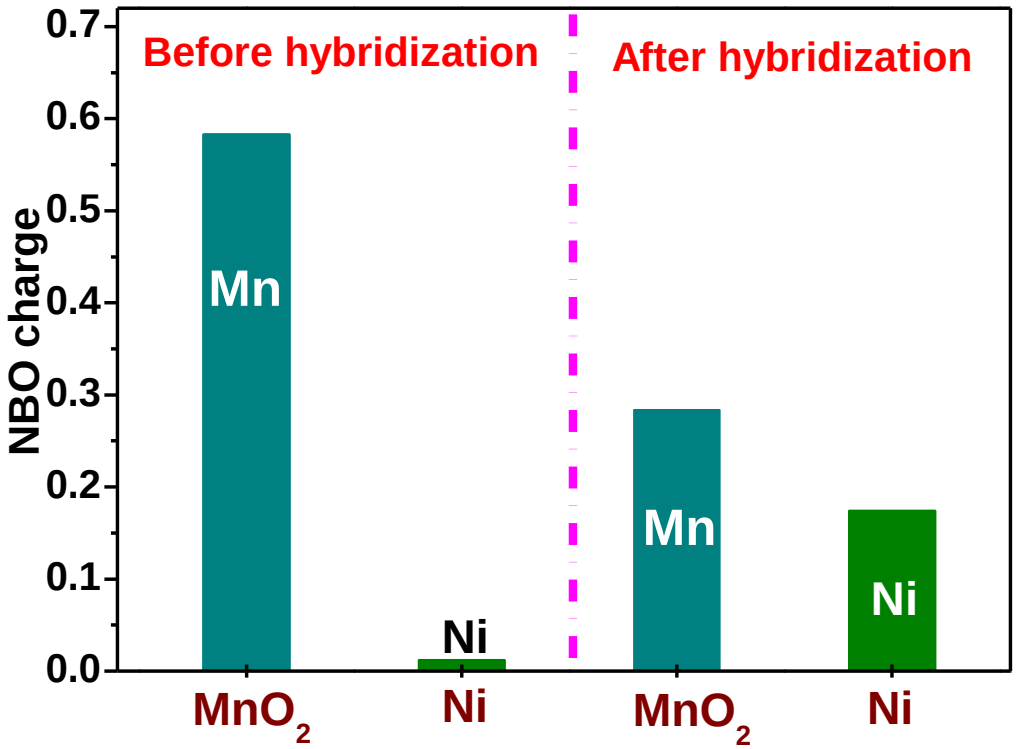

Figure S8. NBO charge distribution of Mn and Ni before and after hybridization.

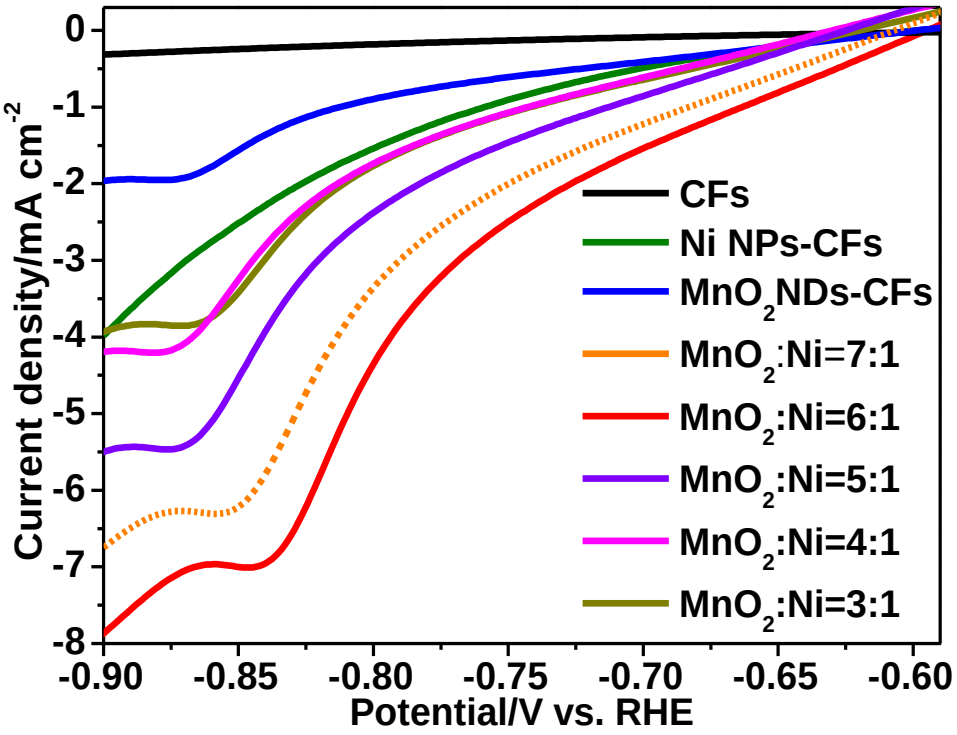

Figure S9. Polarization curves of Ni NPs/MnO_2 NDs-CFs with different mass ratio of MnO_2 and Ni.

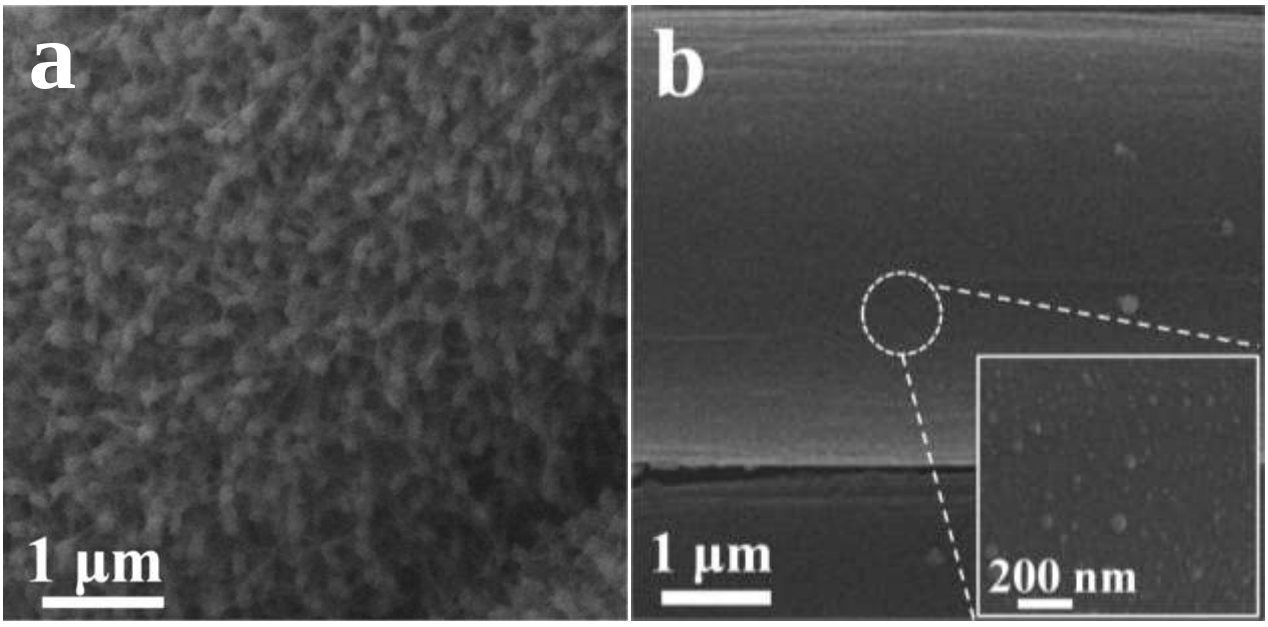

Figure S10. SEM images of (a) MnO_2 NDs-CFs; (b) Ni NPs-CFs.

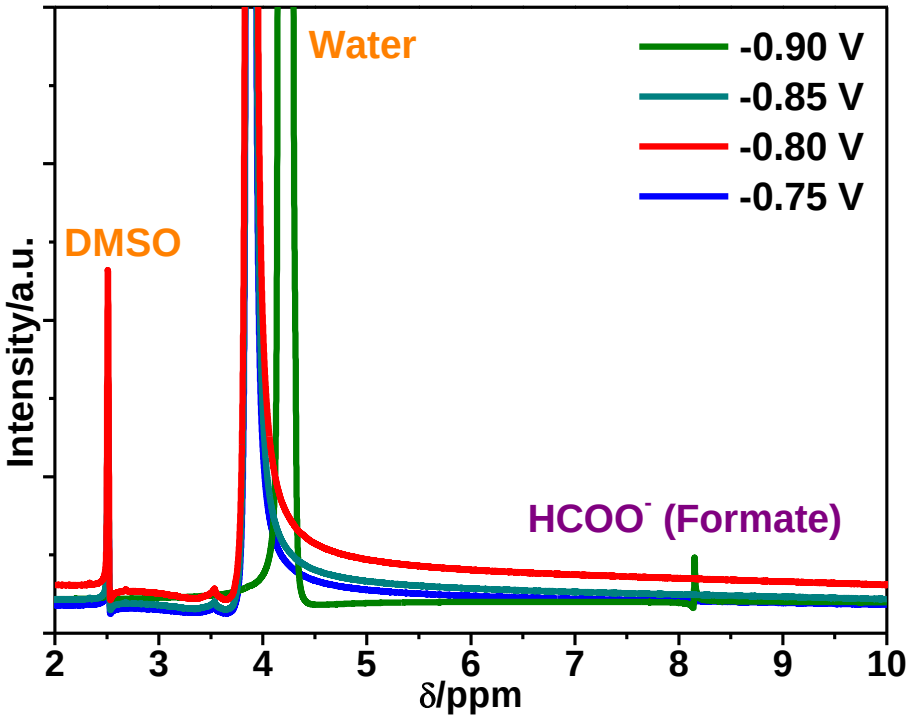

Figure S11. ^{1}H NMR spectra of the electrolyte after CO_2 reduction by Ni NDs-CFs at the potential from -0.75 to -0.90 V.

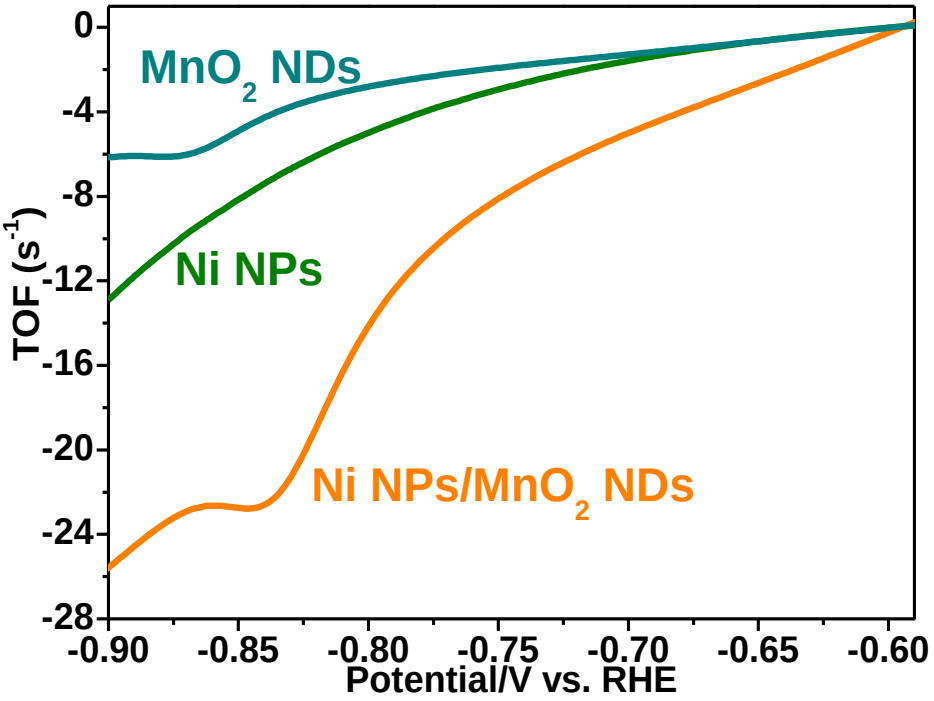

Figure S12. TOFs of Ni NPs/MnO_2 NDs-CFs, MnO_2 NDs-CFs, Ni NPs-CFs and CFs as a function of overpotential.

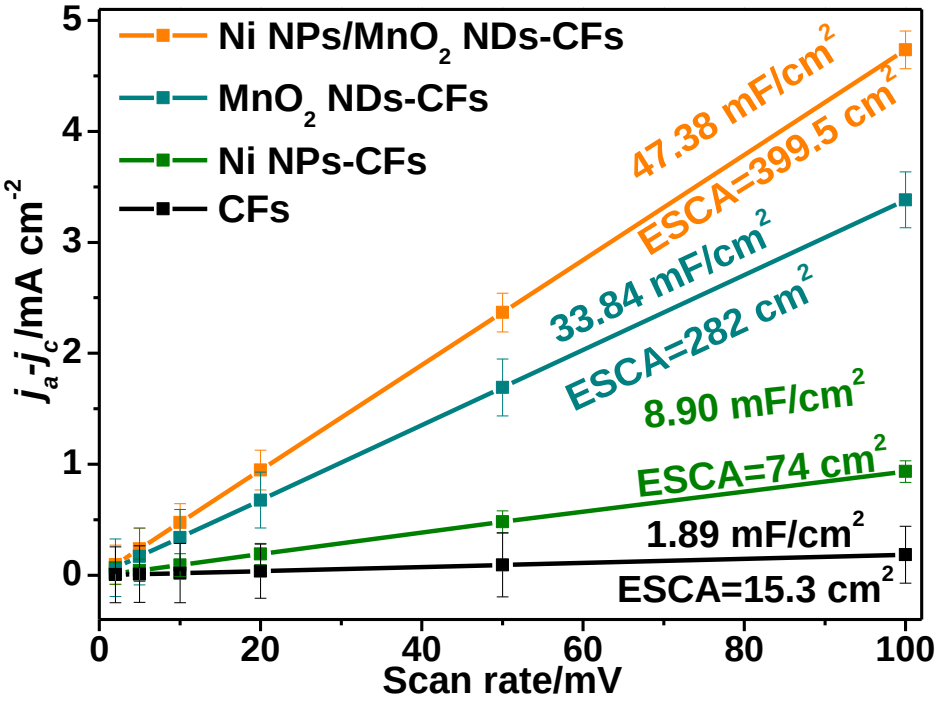

Figure S13. Charging current density differences j_a-j_c plotted against scan rates of the Ni NPs/MnO_2 NDs-CFs, MnO_2 NDs-CFs, Ni NPs-CFs and CFs electrocatalysts.

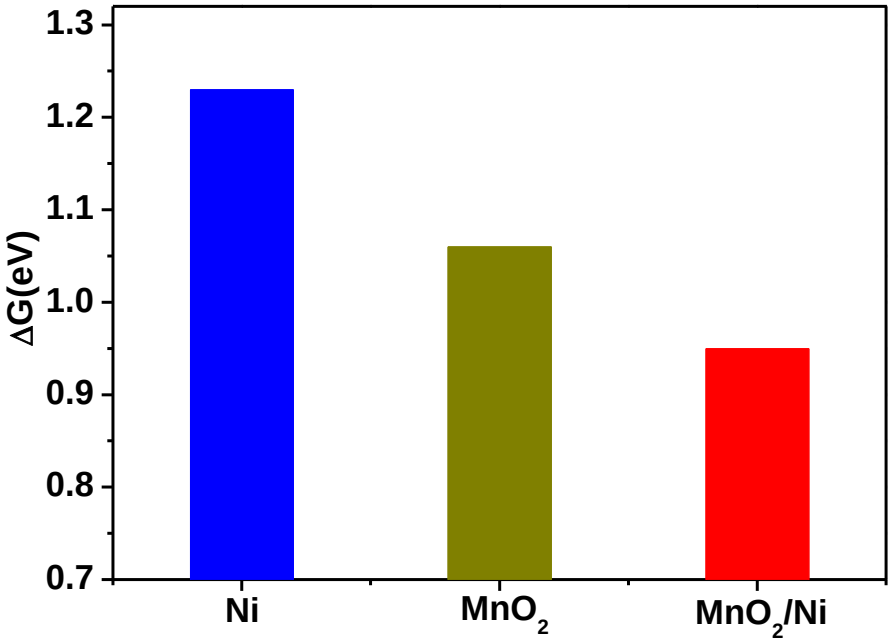

Figure S14. DFT calculations of MnO_2, Ni and MnO_2/Ni for the free energy barrier of equation (1).

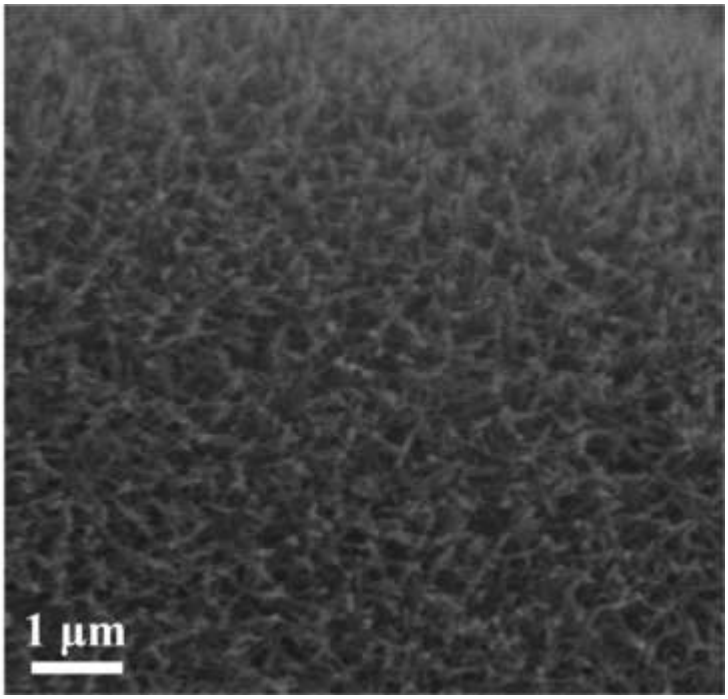

Figure S15. SEM image of Ni NPs/MnO_2 NDs-CFs after 40000 s at -0.84 V *vs.* RHE.

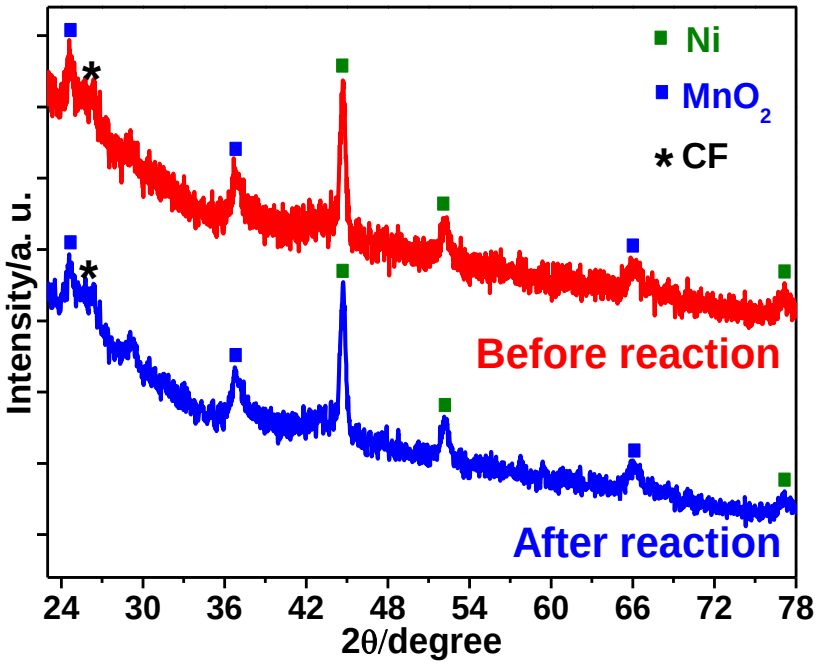

Figure S16. XRD patterns of Ni NPs/MnO_2 NDs-CFs before and after 40000 s at -0.84 V *vs.* RHE.

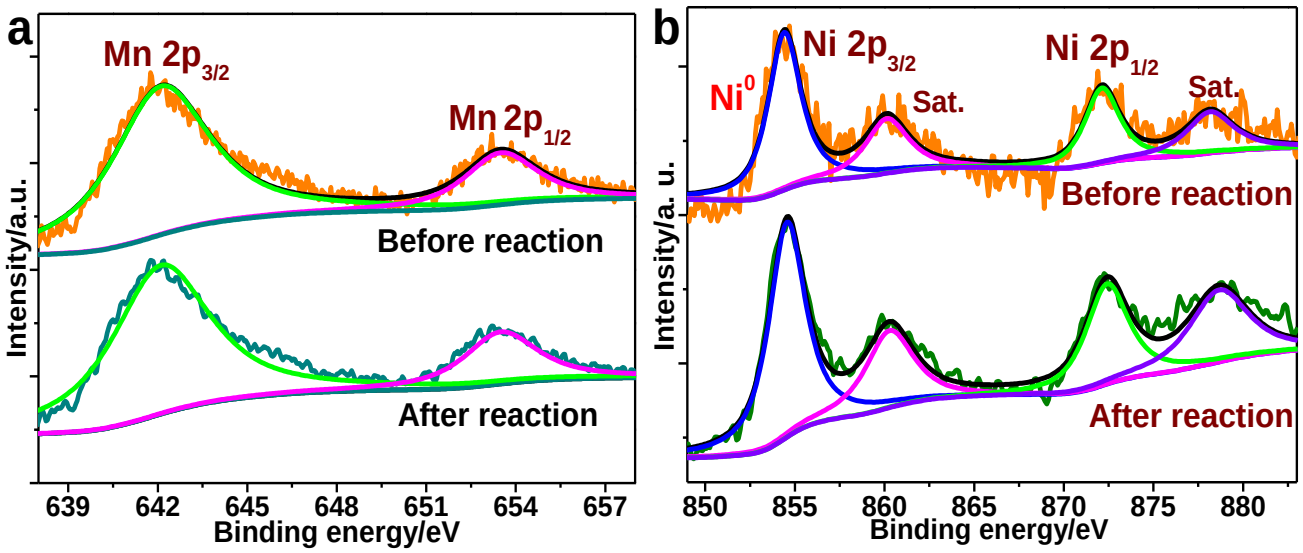

Figure S17. XPS spectrum of (a) Mn 2p and (b) Ni 2p of Ni NPs/MnO_2 NDs-CFs before and after 40000 s reaction under -0.84 V *vs.* RHE.

Table S1. Comparison of the electrocatalytic activity of Ni NPs/MnO_2 NDs-CFs catalysts with some representative solid-state CO_2 electrochemical reduction catalysts recently reported. (*U*: Overpotential *vs.* $CO_2/HCOO^-$; *j*: Current density at the applied overpotential; *FE*: Faradaic efficiency of formate formation)

Catalyst	*U*/mV	*j*/mA cm^{-2}	*FE*/%	Reaction time/s	Reference
Ni NPs/MnO_2 NDs-CFs	**230**	**7.25**	**85.5**	**100000**	**Our work**
Sn/SnO_x	390	0.60	19	43200	Ref 1
Pd nanoparticles decorated CNT	200	1.0	65	9000	Ref 3
Partly reduced Co_3O_4	240	10.6	91	216000	Ref 7
Cu_2O film	450	7.5	40	3600	Ref 9
Ultrathin Co_3O_4	270	0.68	64.3	144000	Ref 11
N-CNT+polyethylenimine	850	3.0	83	86400	Ref 12
5 nm Sn	340	5.2	93	64800	Ref 18

*The above references have been listed in paper.