Supporting Information:

Boron Induced Oxygen Vacancy for Methanol Oxidation Reaction: Selective towards Formate via Non-Noble Metal

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Characterization studies

The synthesized electrocatalyst materials was characterized through various techniques to identify the composition, morphology, etc. In order to identify the phase purity of the composite PANaltical X'pert powder diffractometer was employed by using Cu Kα radiation (λ=1.5406Å) source. Field emission scanning electron microscopy (FE-SEM) (FEI Quanta FEG 200) and transmission electron microscopy (TEM) JOEL operated at 200 kV was used to study the morphology of the prepared sample. The composition of the composite was examined using FTIR and X-ray photoelectron spectroscopy (XPS) by using K-Alpha XPS System (Thermo Scientific) and SHIMADZU IR TRACER-100. The Electron Spin Resonance measurement were performed using JES-FA200. ^{1}H and ^{13}C NMR spectroscopy was used to find the intermediate species.

Electrochemical studies

The Electrochemical studies such as cyclic voltammetry (CV), chronoamperometry (CA) and impedance spectra were performed with Biologic SP150 instrument. The electrochemical analysis was adopted by using three-electrode configuration with glassy carbon (GC), platinum (Pt) wire and silver/silver chloride (Ag/AgCl) electrode as working, counter and as reference electrodes, respectively. All the measurements were carried out in 1M KOH and 1M methanol. In order to fabricate the sample on the electrode surface, the slurry was prepared by following procedure. Initially, 2.5 mg of catalyst was added to 500 ul (1:1) of water/ethanol solution along with binder nafion (5 µl). The prepared slurry was ultrasonicated for 2 hours to obtain uniform dispersion. The slurry was drop casted on GC electrode and left for drying at room temperature.

Computational details:

First-principles density functional theory (DFT) [1] calculations are performed using the Vienna ab initio simulation package (VASP) [2]. The basis set is constructed within projector augmented plane waves [3]. The plane wave cutoff energy is set as 500 eV. The Perdew-Burke-Ernzerh (PBE) functional is used to treat the exchange and correlation functional [4]. All the structures are fully relaxed to obtain a reasonable structure until all forces on every atom are smaller than 0.001 eV/Å. A k-point meshes of 6x6x1 is used for $NiCo_2O_4$ and $B/NiCo_2O_4$ (B substituted in 4 coordinated Co) substrates.

Formula

Diffusion coefficient was calculated using following equation (1)

$$Ipa = 0.4463nFAC\left[\frac{nFvDapp}{RT}\right]^{1/2}$$ -------------------------(1)

whereas, I_{pa} is the anodic peak current density ($mAmg^{-1}$), n denotes the number of electron, F denotes the faradaic constant, C denotes the methanol concentration, v is the scan rate ($V s^{-1}$), R and T are the universal gas constant ($8.314 J K^{-1} mol^{-1}$) and temperature in K, and Dapp is the diffusion coefficient of electroactive species ($cm^2 s^{-1}$).

Faradic efficiency was calculated using following equation (2)

$$F.E = \frac{n * F * no.\, of\, Mole\, formed * V}{Q}$$ --(2)

Whereas, n=No of electron transferred

F: Faradaic constant ($96,485 C mol^{-1}$)

V: Volume of the electrolyte

Q: Total charges passed through the electrode
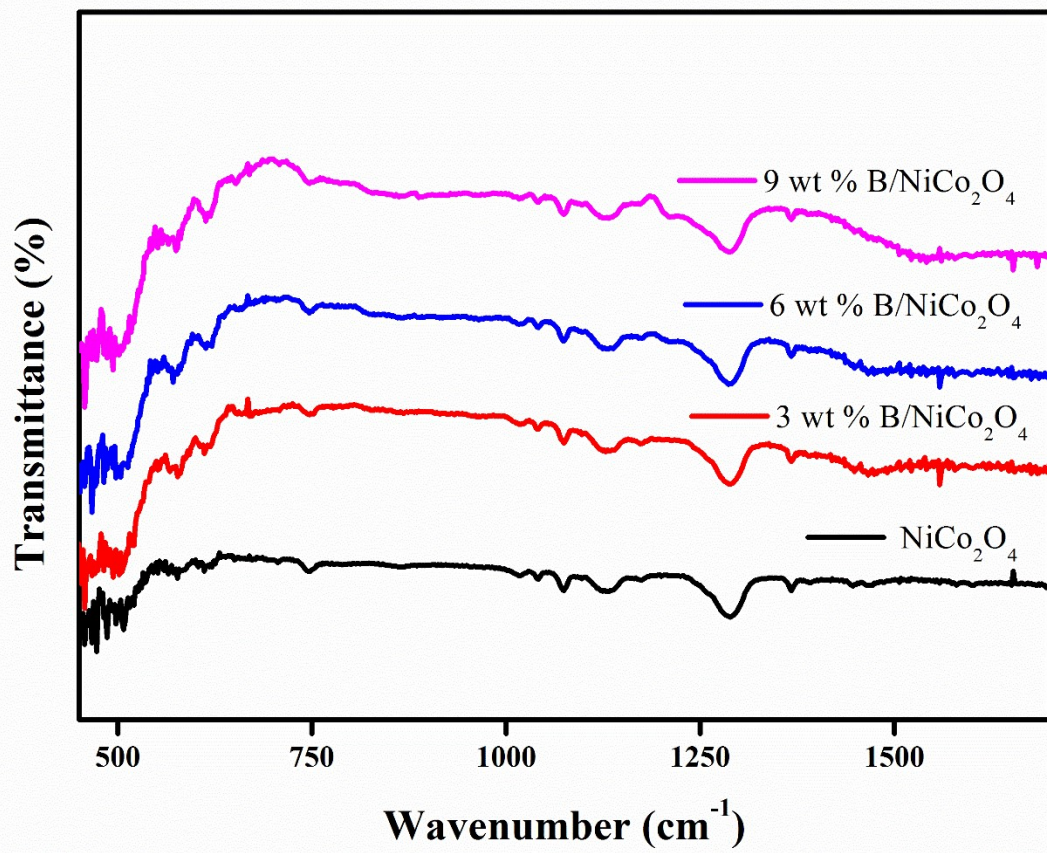
Figure S1: a) FT-IR spectra of $NiCo_2O_4$ and dt (3, 6 & 9) wt. % B loaded $NiCo_2O_4$ composite
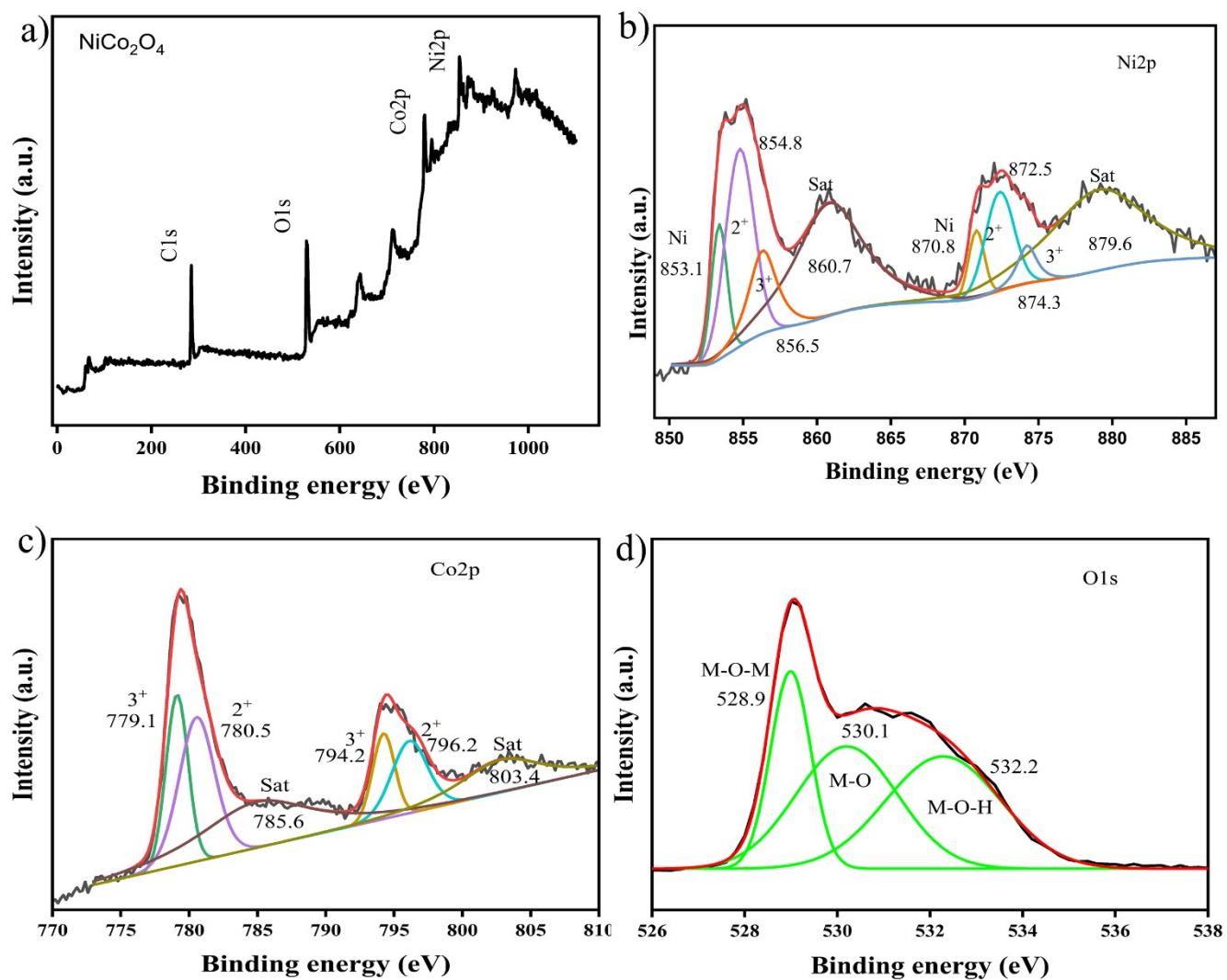
Figure S2: XPS spectra of a) wide spectra, b) Ni2p spectra, c) Co2p spectra and d) O1s spectra of $NiCo_2O_4$
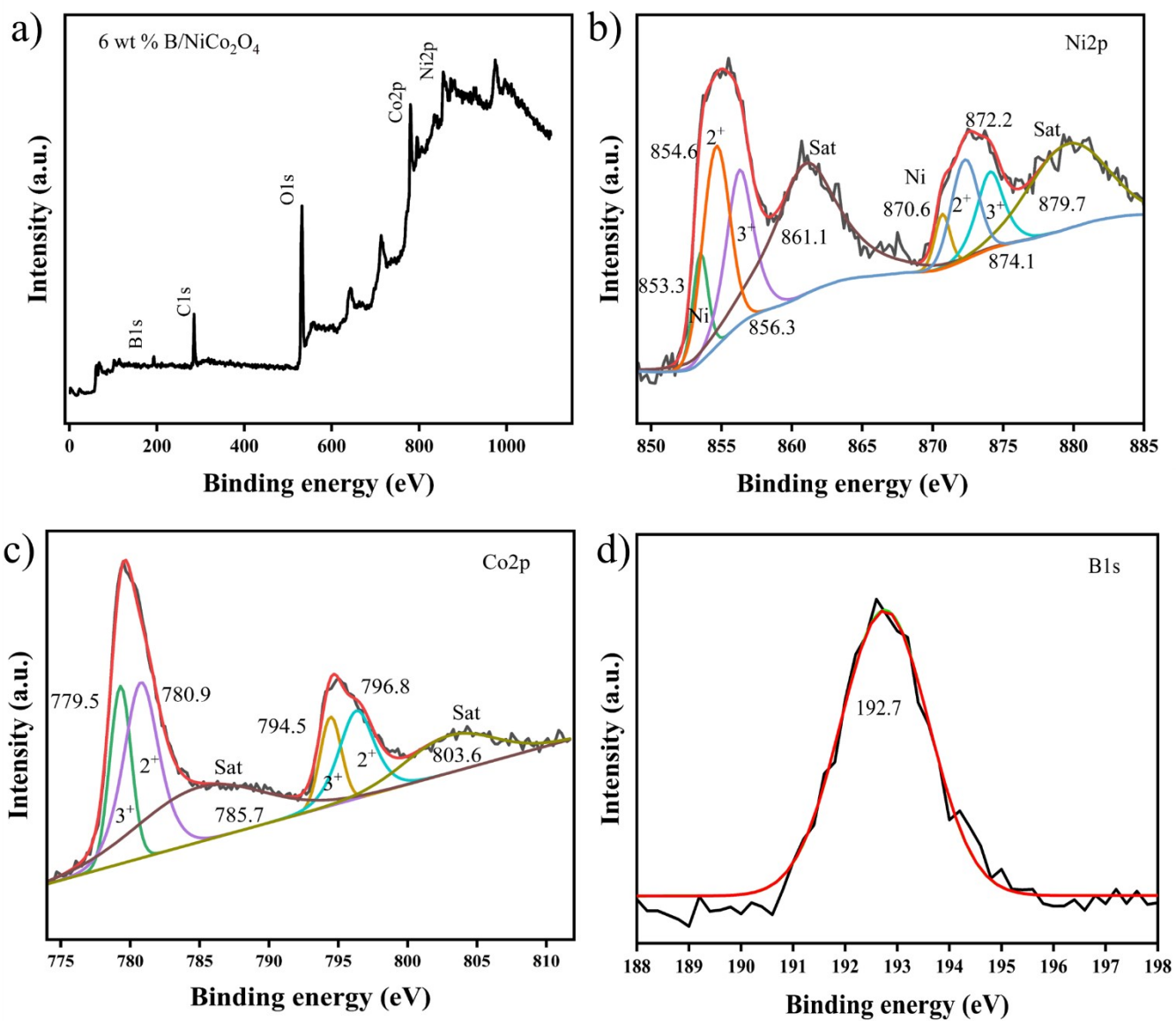
Figure S3: XPS spectra of a) wide spectra, b) Ni2p spectra, c) Co2p spectra and d) B1s spectra, of 6 wt % B/NiCo$_2$O$_4$
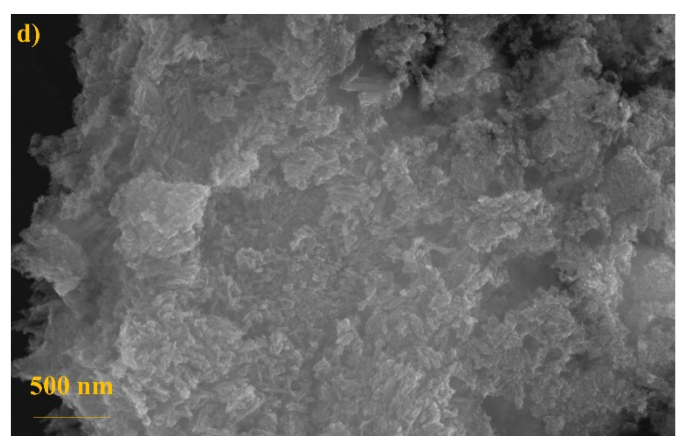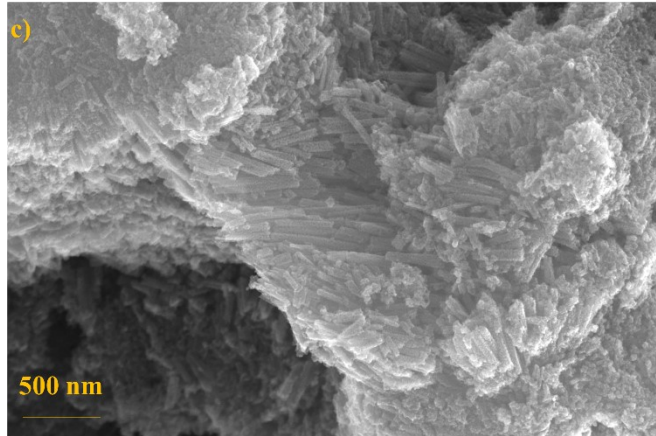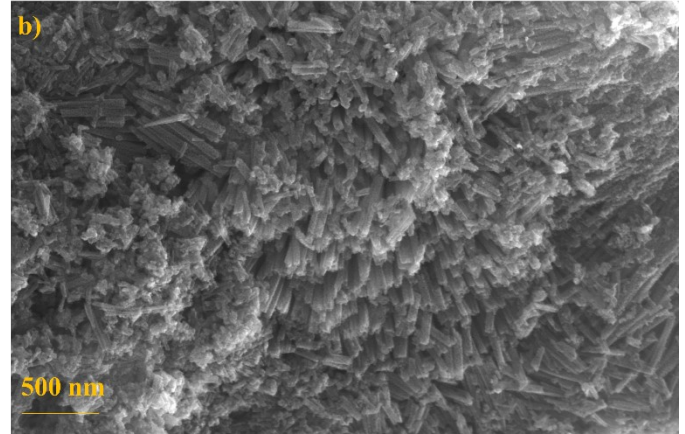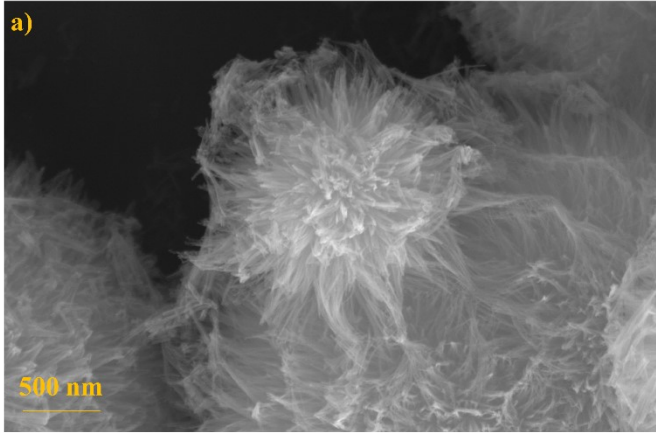
Figure S4: SEM images of NiCo$_2$O$_4$ and dt (3, 6 & 9) wt. % B loaded NiCo$_2$O$_4$ composite
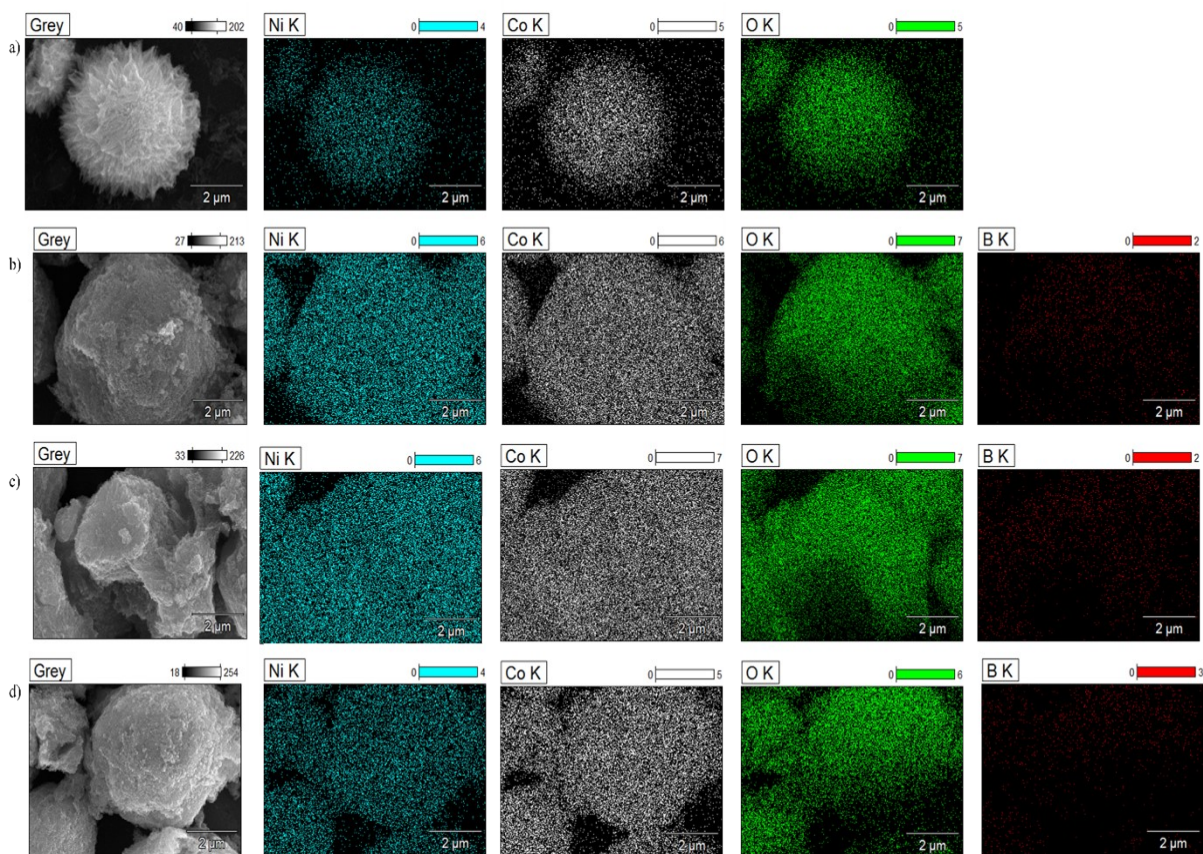
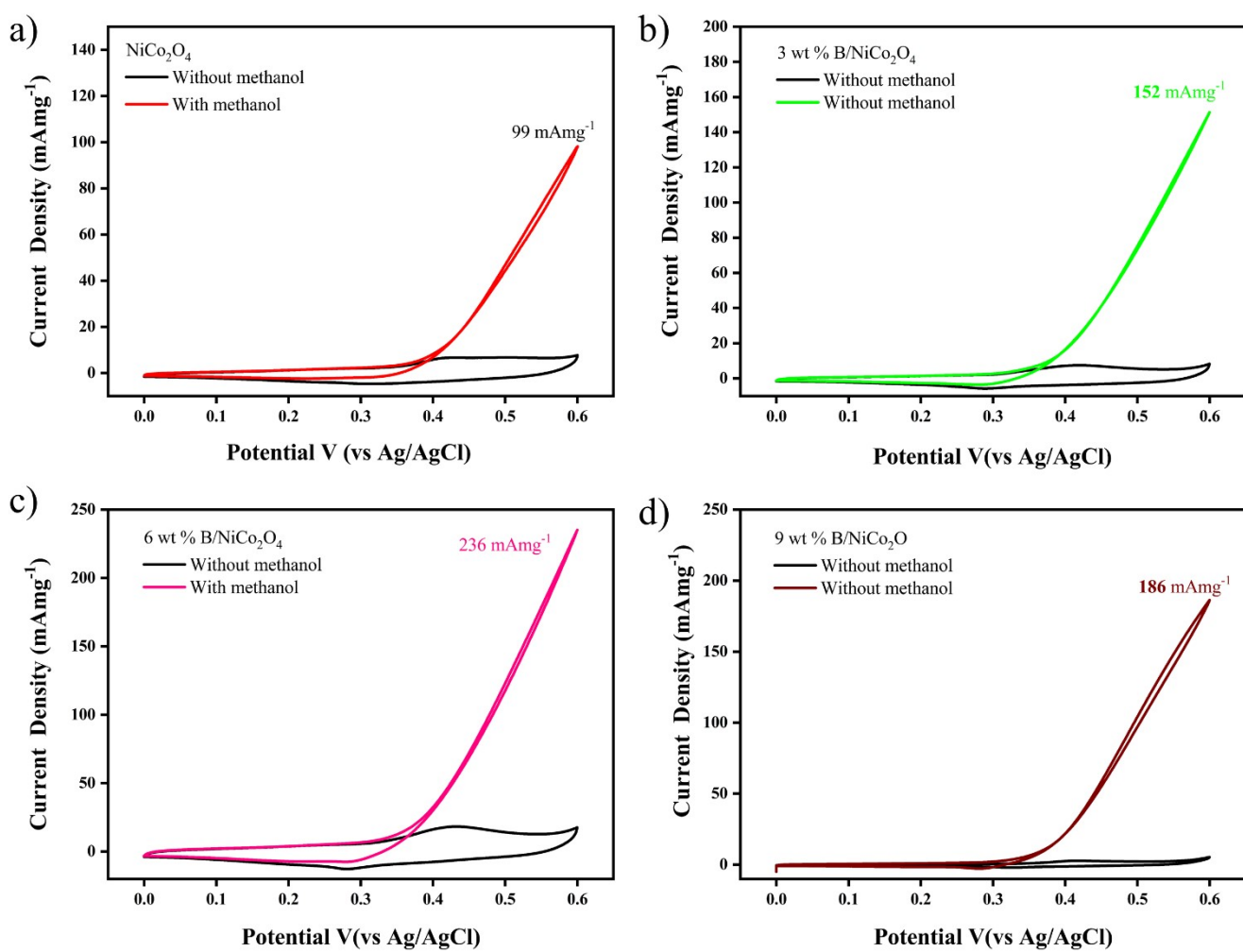Figure S5: SEM-mapping of NiCo$_2$O$_4$ and dt (3, 6 & 9) wt. % B loaded NiCo$_2$O$_4$ composite

Figure S6. a-d) CV curves of NiCo$_2$O$_4$ and dt (3, 6 & 9) wt % B doped NiCo$_2$O$_4$ modified electrodes in 1.0 M KOH and with 1 M MeOH at 50 mV s^{-1}
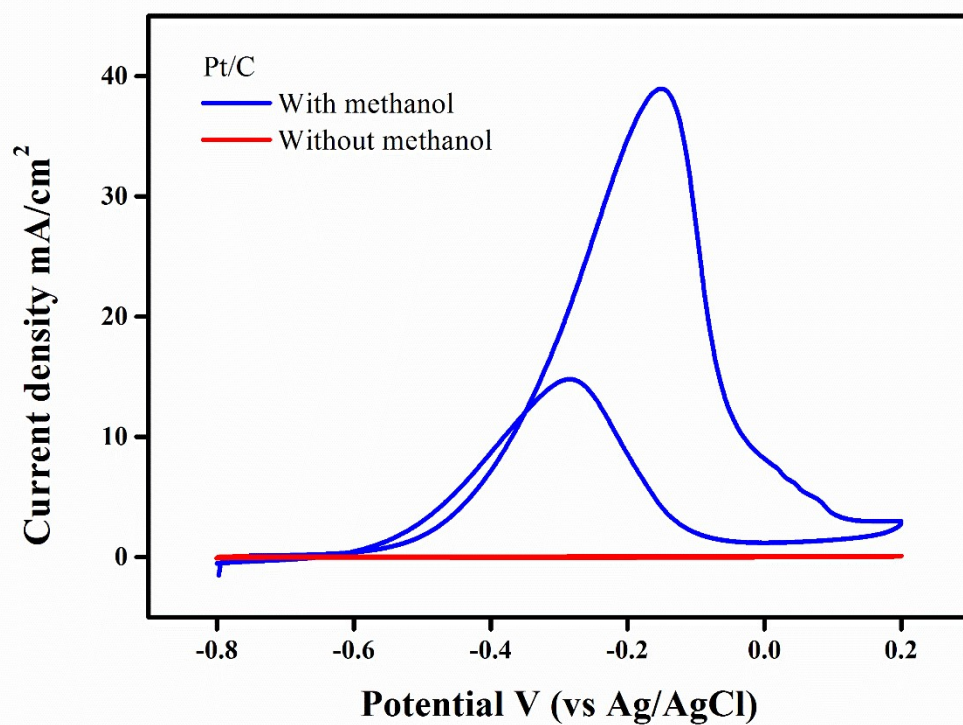
Figure S7. CV curves of commercial Pt/C modified electrodes in 1.0 M KOH with and without 1 M MeOH at 50 mV s^{-1}.
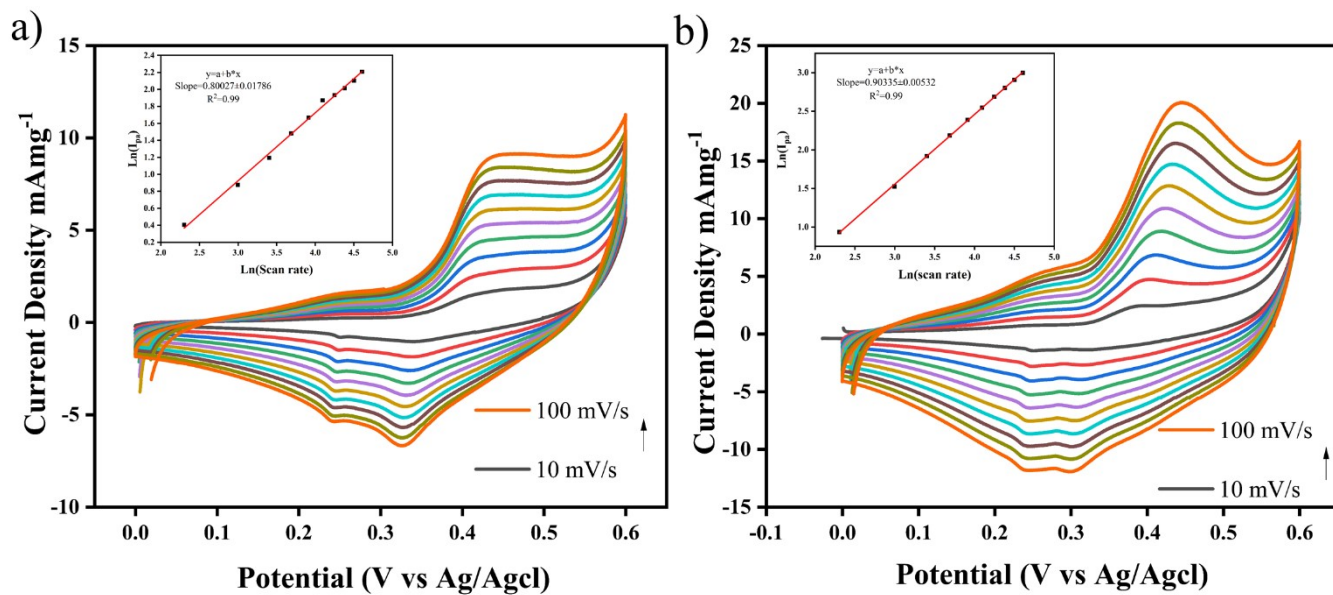
Figure S8: Cv cure of a) pristine b) 6 wt % B/NiCo$_2$O$_4$ electrocatalyst with different scan rate in presence of 1M KOH.
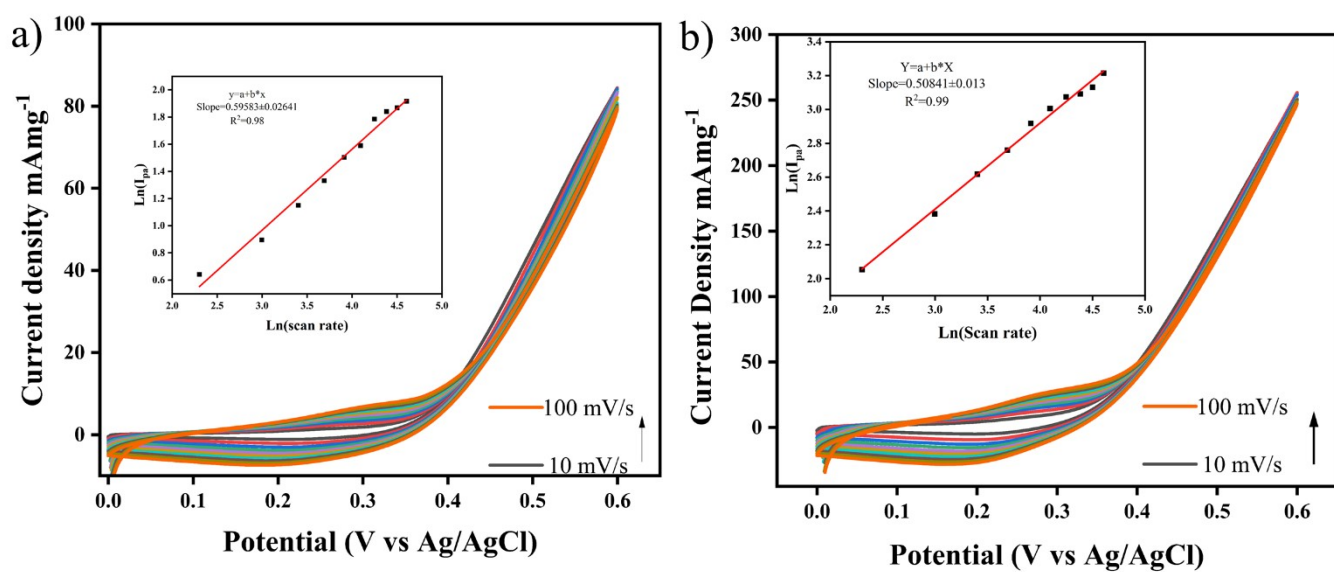
Figure S9: Cv cure of a) pristine b) 6 wt % B/NiCo$_2$O$_4$ electrocatalyst with different scan rate in presence of 1M KOH and 1M MeOH.
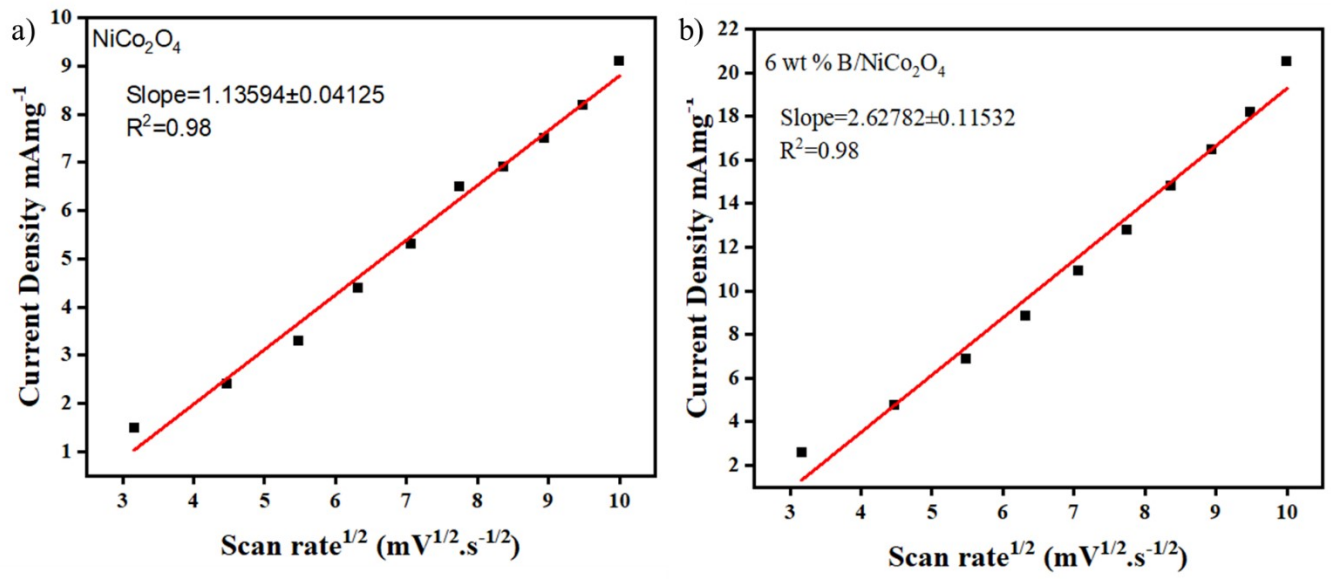
Figure S10: Cv cure of a) pristine b) 6 wt % B/NiCo$_2$O$_4$ electrocatalyst with different scan rate in presence of 1M KOH and 1M MeOH.
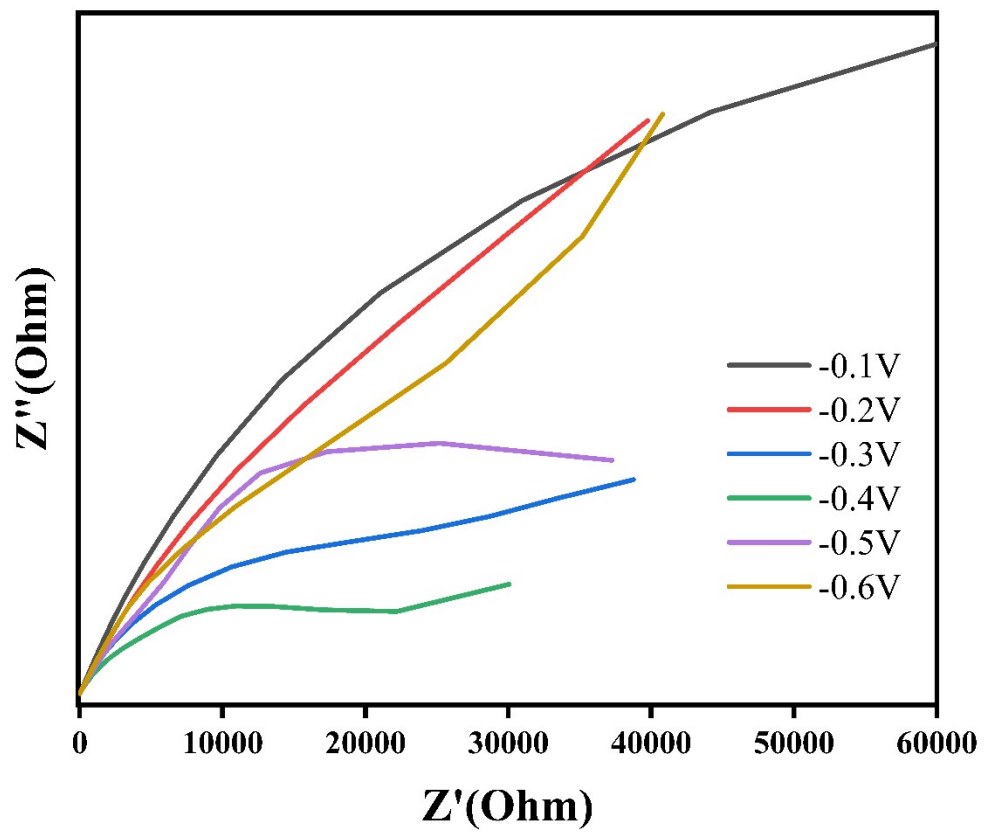
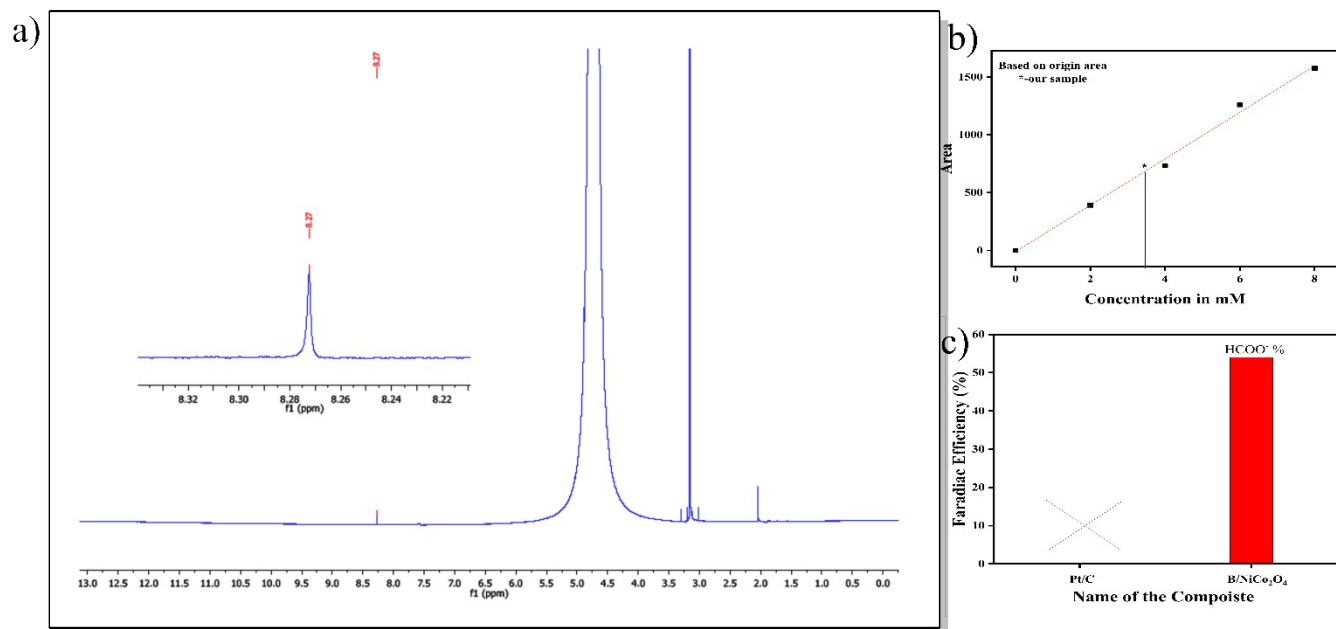Figure S11. Nyquist plot 6 wt % B/NiCo$_2$O$_4$ modified electrodes in 1M KOH + 1M MeOH with different potential.

Figure. S12: ^{1}H NMR spectra, b) Quantitative analysis of known formate, c) Faradaic efficiency of Pt/C and 6 wt % B/NiCo$_2$O$_4$.
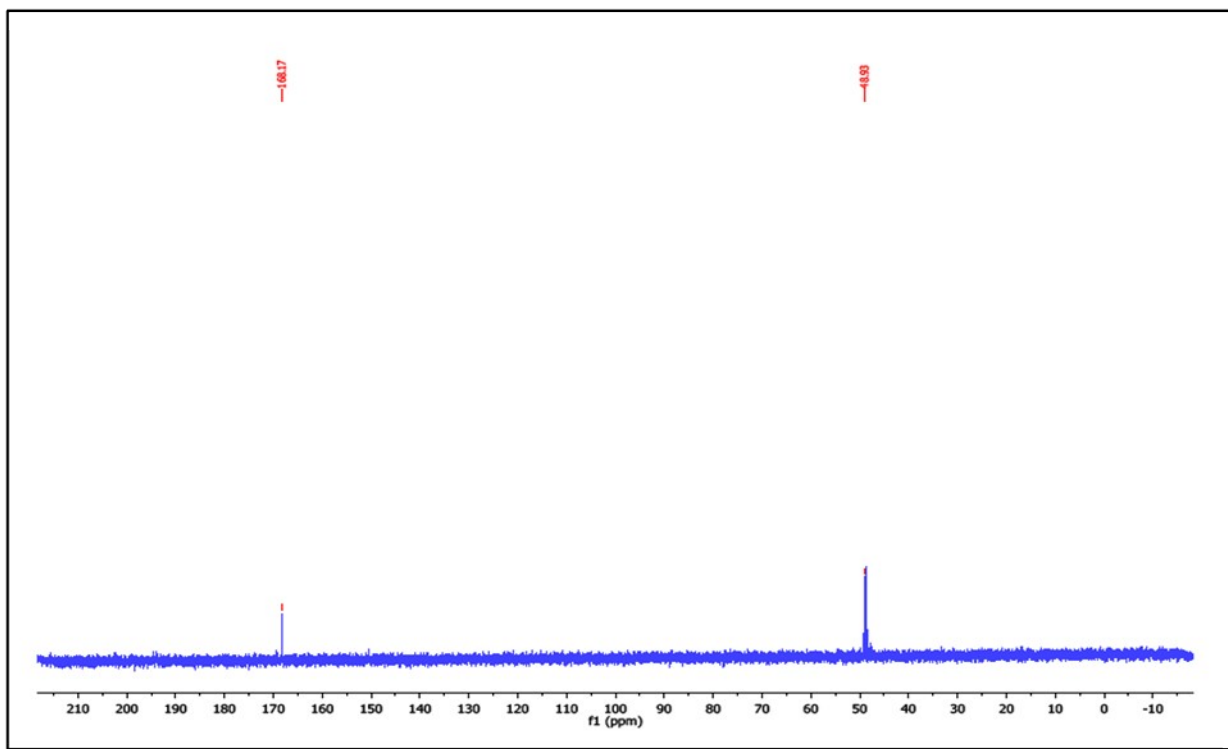
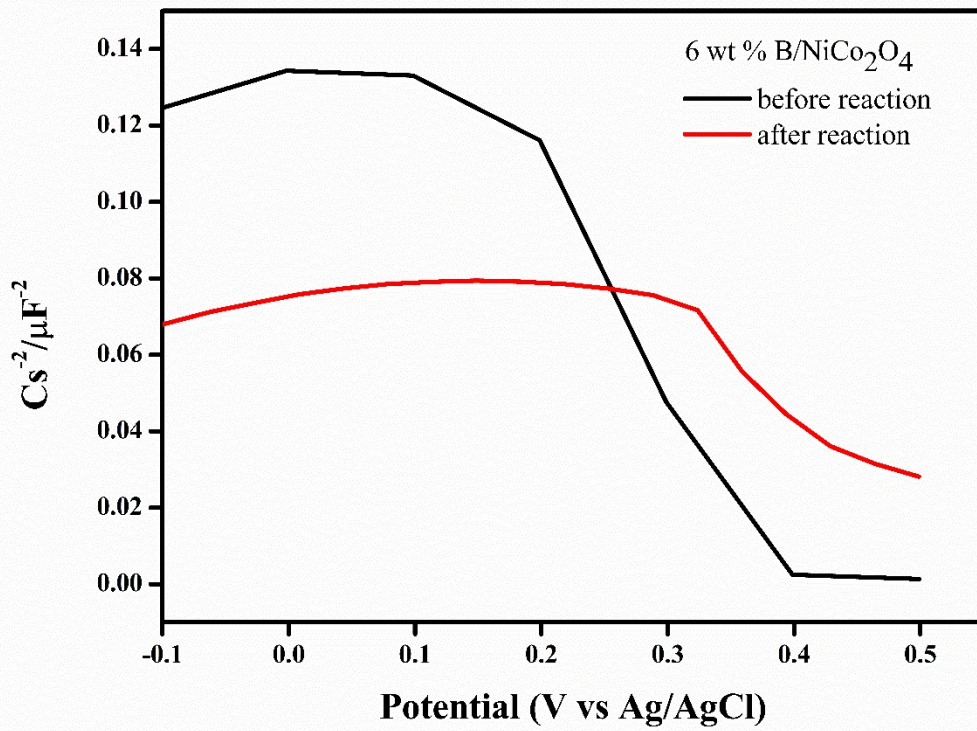Figure S13. C^{13} NMR spectra of 6 wt % B/NiCo$_2$O$_4$

Fig S14: Mott Schottky analysis of 6 wt % B/NiCo$_2$O$_4$ (before and after reaction) in 1 M KOH and 1 M MeOH.

Table S1: TEM-EDX spectra of 6 wt % B/NiCo2O4 (before and after reaction)

Sample name 6 wt % B/NiCo$_2$O$_4$	Ni	Co	O	B	C
before reaction	6.59	13.74	11.84	4.82	63.01
after reaction	6.17	11.68	10.58	4.62	66.95
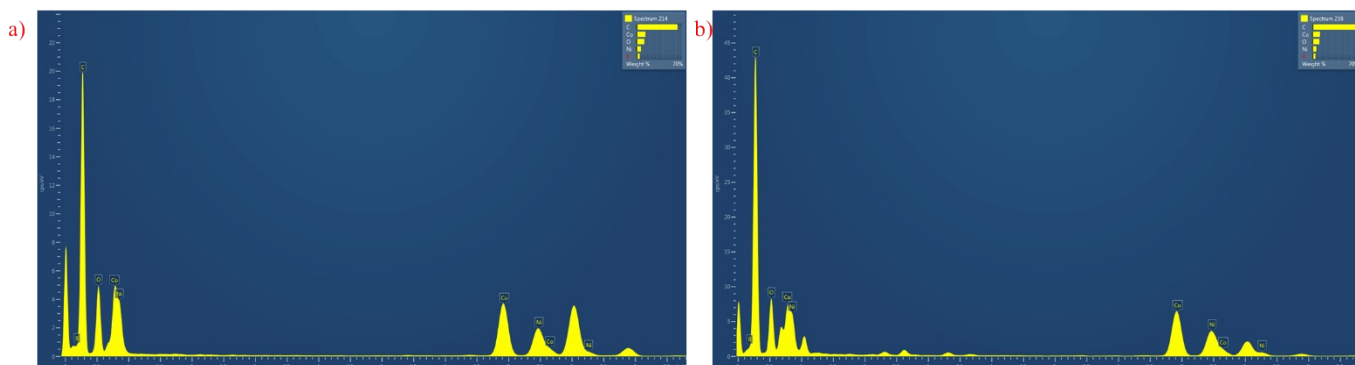
Fig S15: TEM-EDX spectra of 6 wt % B/NiCo$_2$O$_4$ a) before and b) after reaction in 1 M KOH and 1 M MeOH.

(a) NiCo$_2$O$_4$

(b) B/NiCo$_2$O$_4$

Co (C.N.= 4)   Co (C.N.= 6)   Ni   B   O   O - vaccancy

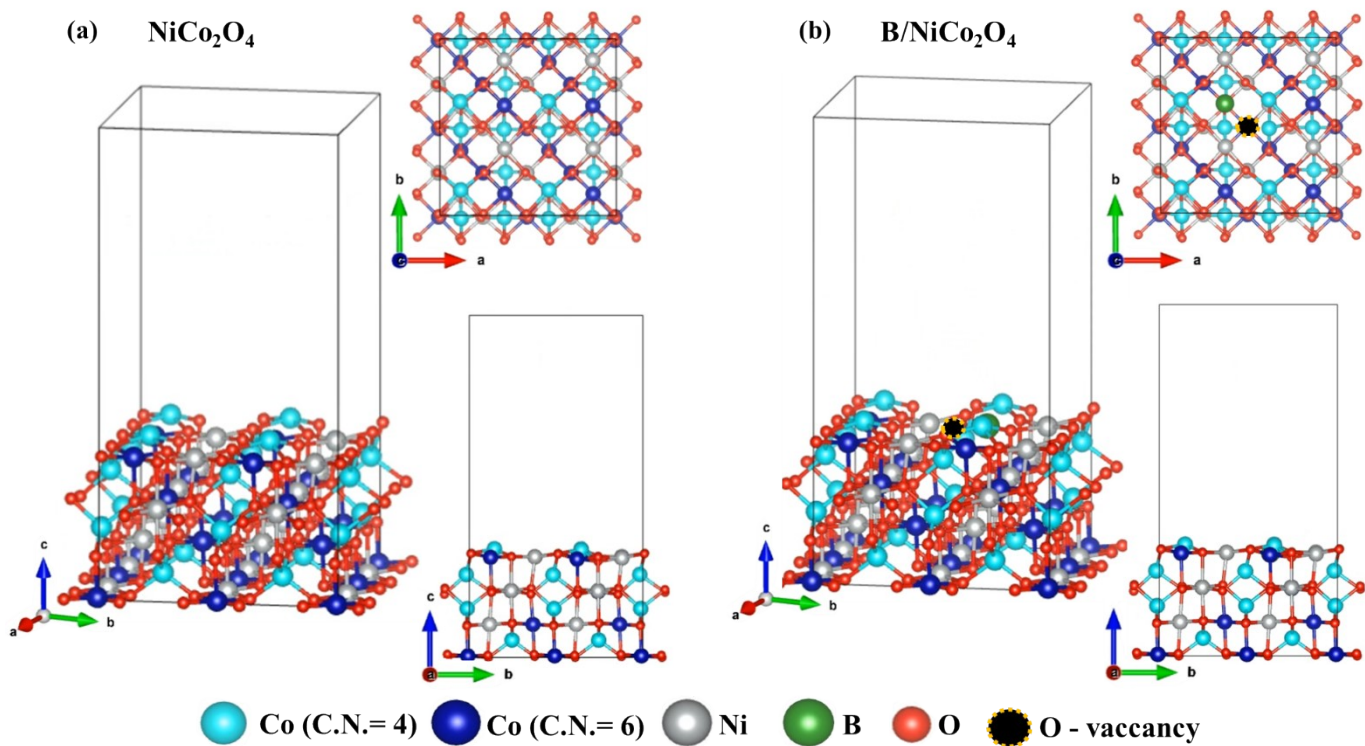Figure S16. Optimized structure of a) NiCo$_2$O$_4$ and b) B/NiCo$_2$O$_4$ substrates along (001) plane. Here, the light blue, dark blue, gray, green, red colors and black indicate Co with 4 coordination number, Co with 6 coordination number, Ni, B, O and O-vacancy atoms respectively.
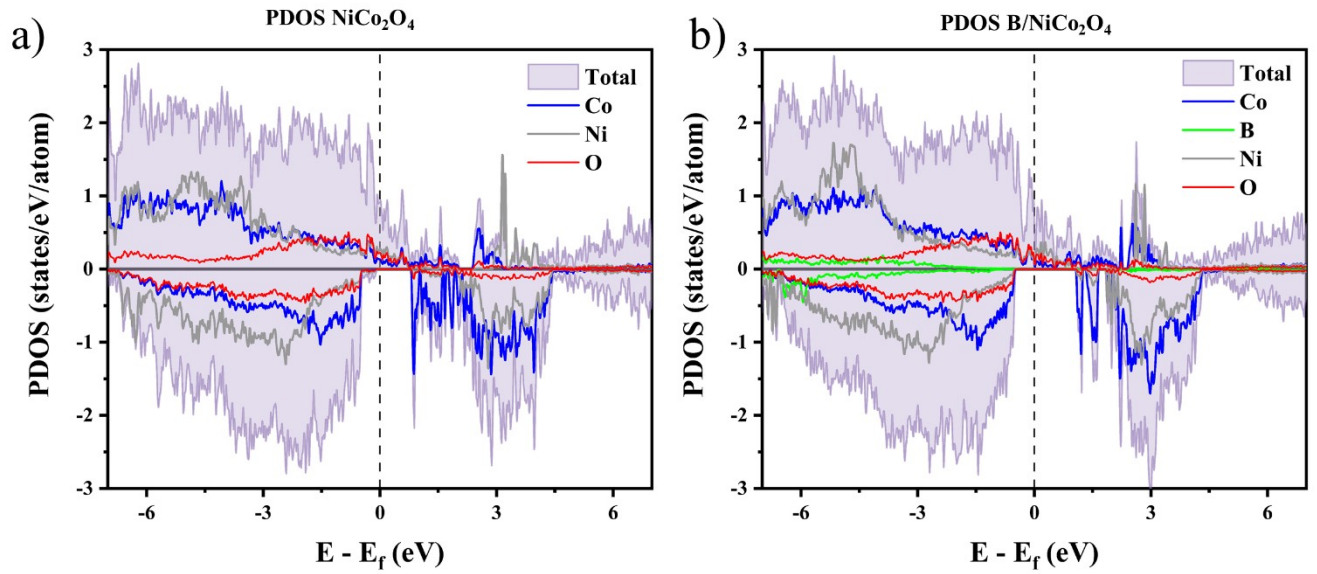
Density of States

Figure S17. PDOS plot of NiCo$_2$O$_4$ and 6 wt % B doped NiCo$_2$O$_4$

Reference:

1. P. Hohenberg and W. Kohn, *Phys. Rev*, 1964, **136**, B864.

2. G. Kresse and J. Furthmüller, *Physical review B*, 1996, **54**, 11169.

3. P. Blochl and E. Bl, *Phys. Rev. B, Condens. Matt*, 1994, **50**, 0163.

4. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865.