Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrodeposited- hydroxide surface covered porous NiCo alloy electrodes for efficient Oxygen Evolution Reaction

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Experimental section

Electrochemical fabrication of porous NiCo alloy electrodes

All the chemicals used in this study were of analytical grade, purchased from Alfa Aesar and used without any further purification. In this typical electrosynthesis, three different molar ratios of Ni + Co metal ion concentrations were used. Wherein, nickel ion concentration (1M) and other electrolytic compositions were kept constant then cobalt ion content was added about 50, 200, 500 milli molars into the each electrolytic bath.

Electrolyte composition:

Nickel chloride - 1M

Cobalt chloride - 50 mM, 200 mM, 500 mM (Bath I, II, III respectively)

Boric acid - 0.5 M

Glycine - 0.5 M

After mixing all the components, it was allowed to stirring of about one hour in order to get a homogeneous solution. To understand the nucleation mode, electrodeposition is carried out by galvanostatic as well as potentiostatic methods. All the deposition process has been done at the temperature of 60 ^{0}C by the use of temperature controller. All the deposition process was carried out with 0.1 mm copper foil and used as a working electrode without any heat treatment.

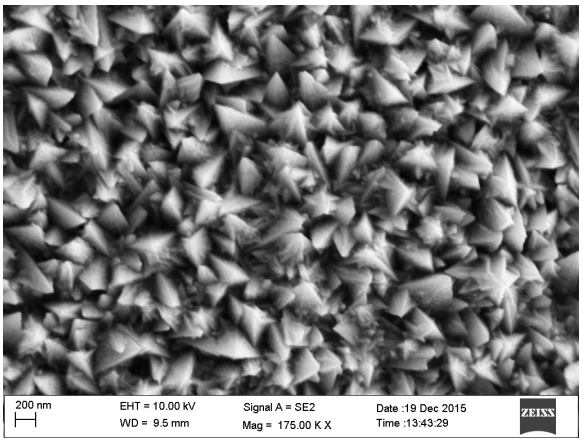
Characterization

Morphology and elemental composition were studied by Field Emission Scanning Electron Microscopy (FESEM) and X-ray energy dispersive spectroscopy (EDS) were obtained from ZEISS SUPRA 55VP coupled with OXFORD X-MAX 20 mm^2. The crystallographic studies of the electrode samples were collected using X-ray diffraction with Cu Kα irradiation (λ = 1.5406 Å). To understand the compositional as well as surface nature information was probed by X-Ray Photoelectron Spectroscopy (XPS, ESCALAB 250) with Al Kα mono chromatic flood and Mg Kα radiation (1253.6 eV) with a double pass cylindrical mirror analyzer. Atomic Force Microscopy was used to measure the surface roughness of the electrode surface.

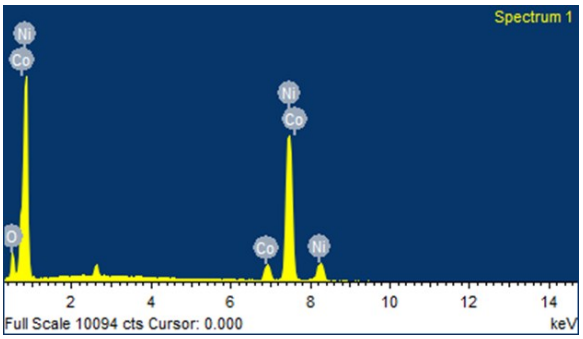
Electrochemical measurements

The NiCo alloy coated copper foils were used as working electrodes, 1x1 cm^2 platinum foil and Hg/HgO (For OER study) were used as counter and reference electrodes respectively. For the electrodeposition process, saturated calomel electrode is used as the reference electrode. A conventional three-electrode set up was used for this study. All the electrochemical experiments were investigated with AUTOLAB galvanostat/ potentiostat. Cyclic voltammetry, Linear sweep voltammetry, and Tafel slopes were used for the evaluation of OER performance. OER polarization curves were obtained at a scan rate of 5 mV/s without iR correction. Electrochemical Impedance spectroscopy (EIS) measurements were recorded by applying an AC voltage with 10 mV amplitude in the frequency range 10^5 to 0.01 Hz.

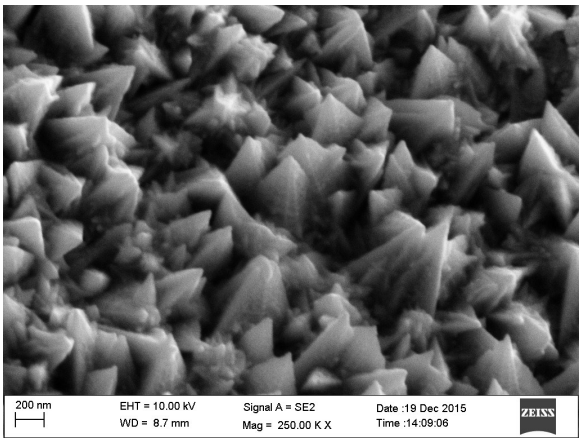
Fig. S1. FESEM (with EDS) images of NiCo nanopyramid and star like morphology



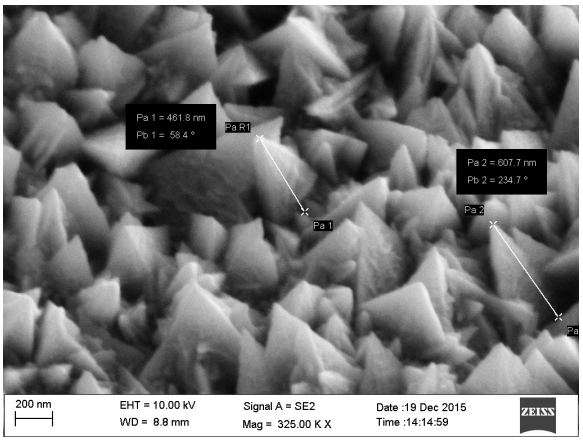
Normal view



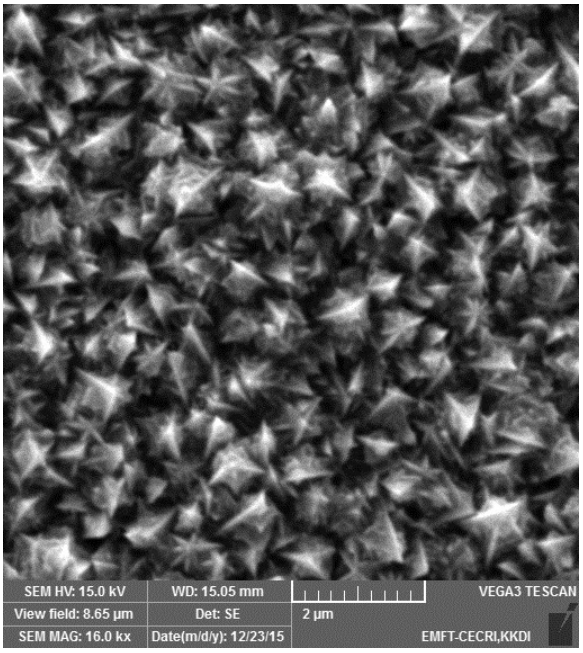
Co – 24 %
Remaining Ni

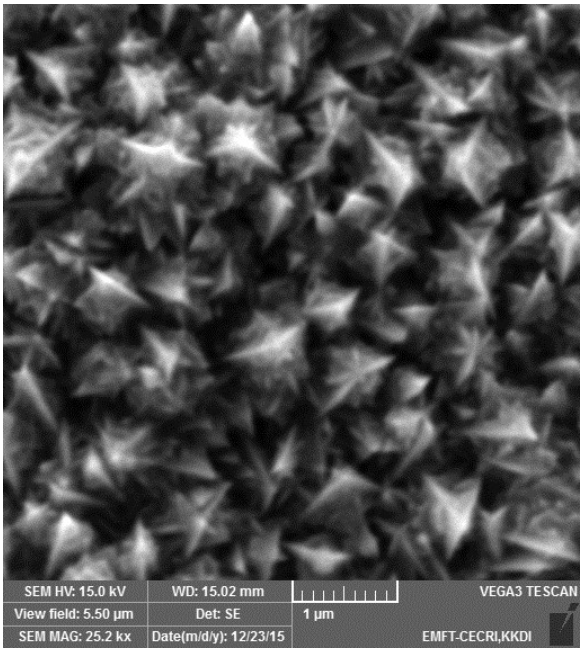


30 degrees tilted

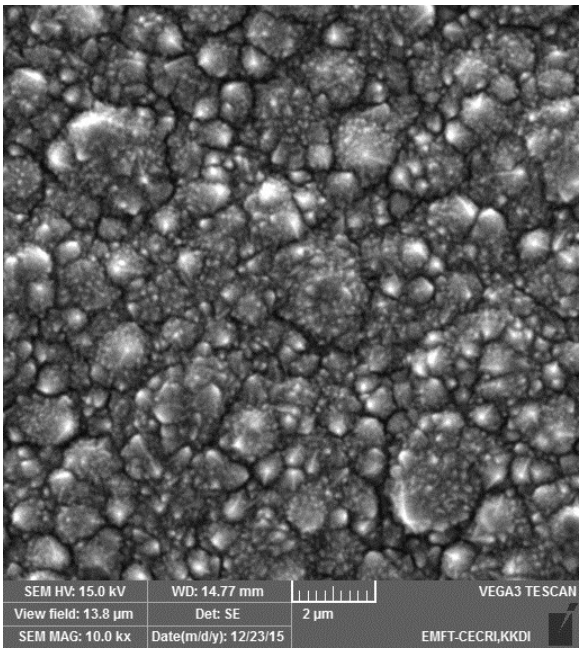


50 degrees tilted

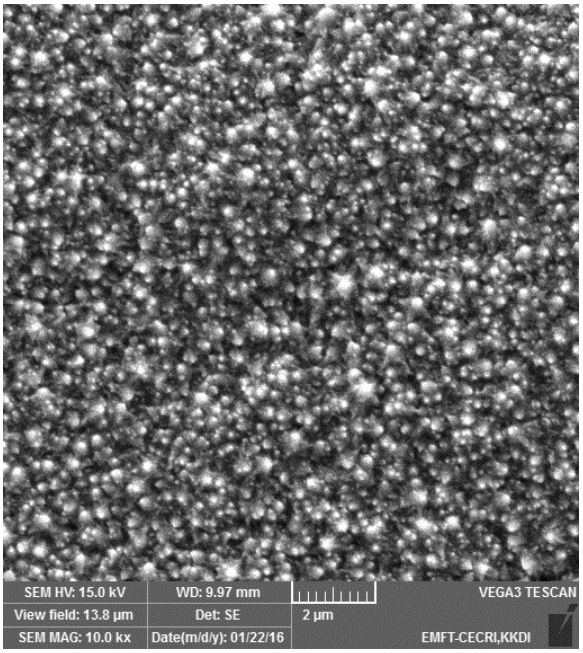




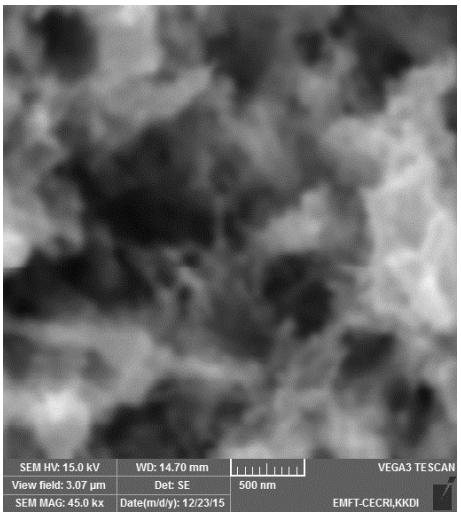
Star like morphology of NiCo alloy (obtained while increasing the deposition time up to 30 minutes in galvanostatic mode)

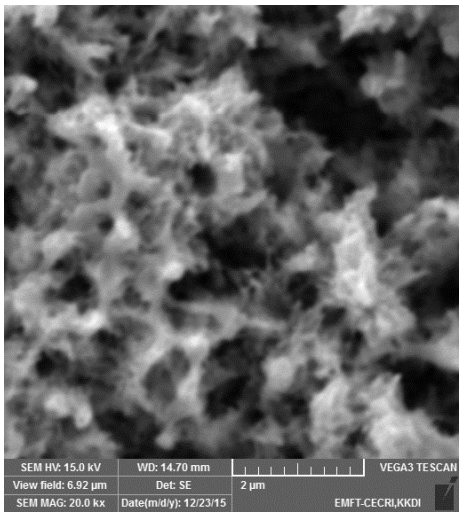


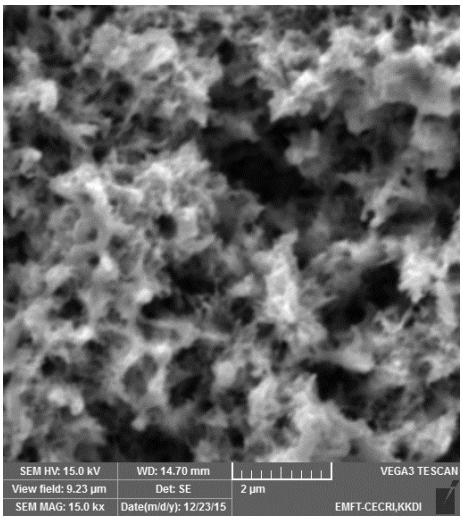
NiCo alloy deposited potentiostatically at -1 V

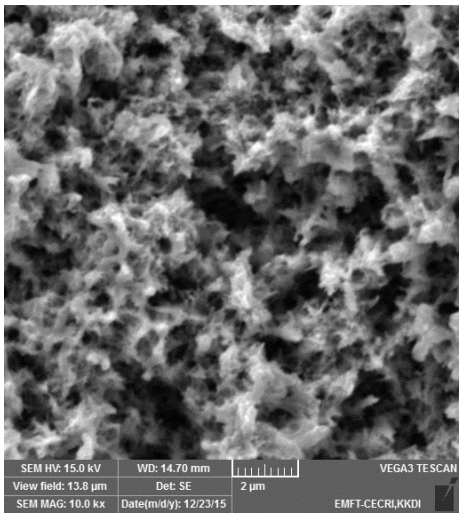


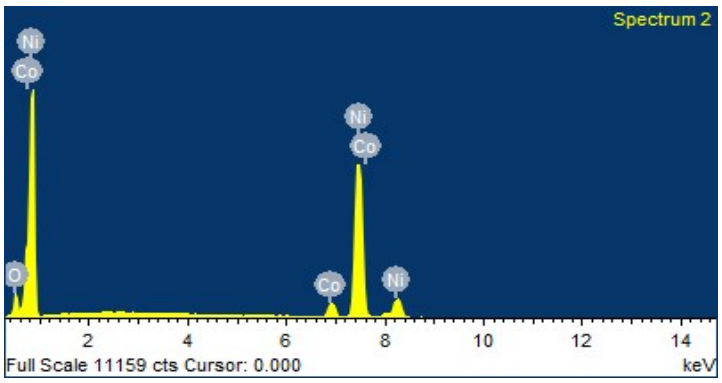
NiCo alloy deposited potentiostatically at -1.2 V







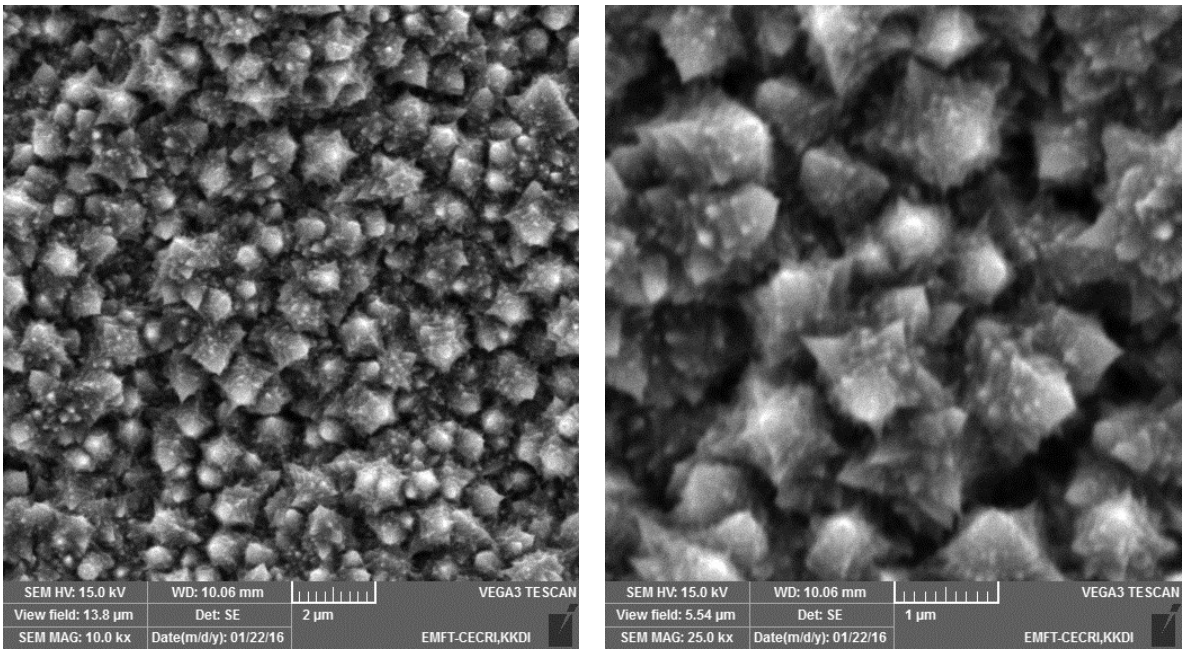




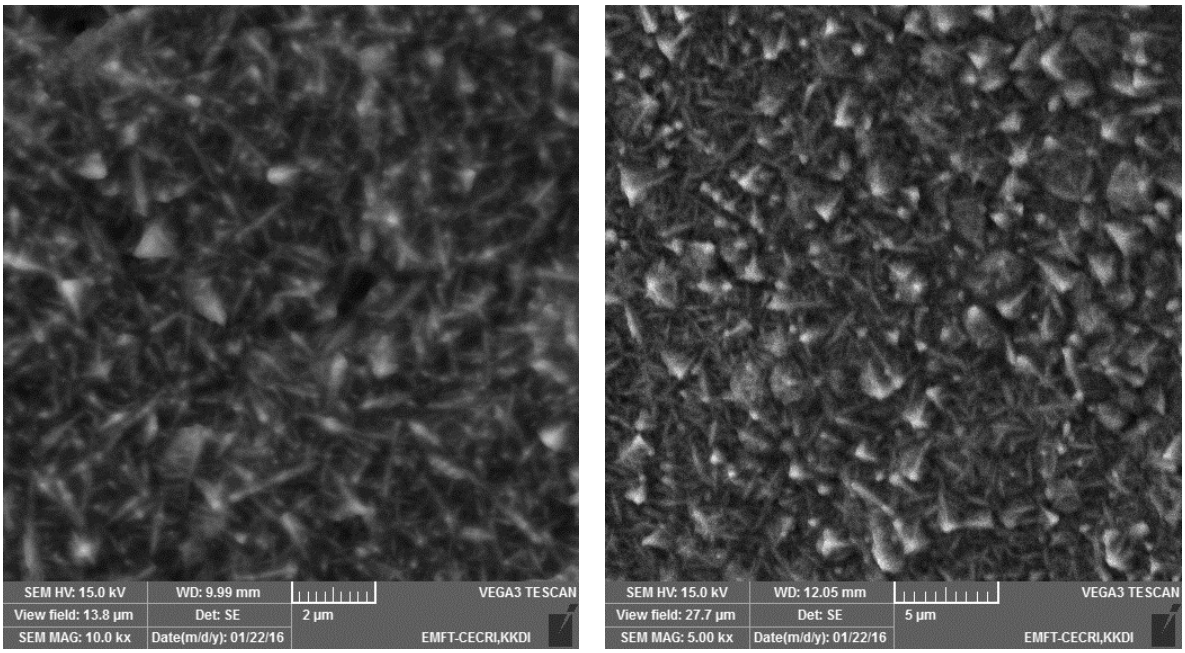
Co – 8 %
Remaining - Ni

NiCo alloy deposited potentiostatically at – 1.4 V

(Images with different magnifications)



SEM images of NiCo alloy (Corn like morphology) deposited from the electrolyte containing 0.2 M cobalt content.



SEM images of NiCo alloy deposited from the electrolyte containing 0.5 M cobalt content.

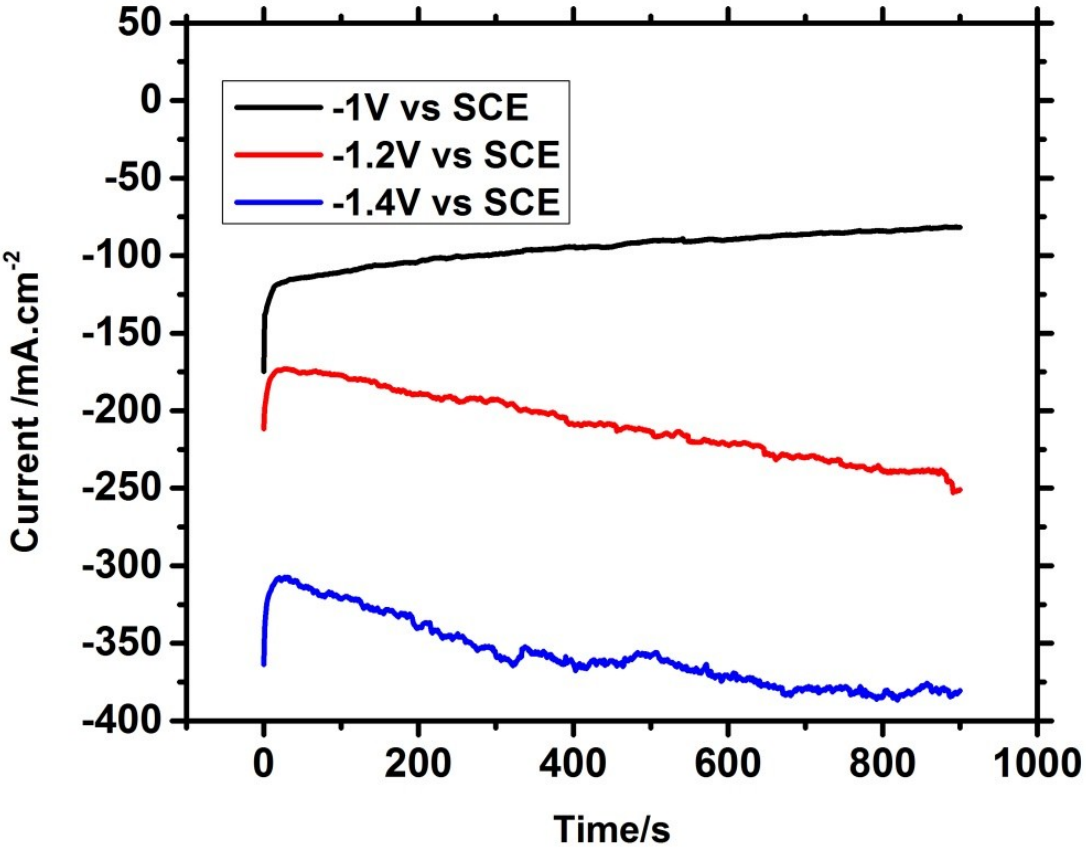


Fig. S2. Potentiostatic deposition of NiCo alloy from the electrolyte containing 0.05 M cobalt content

In these curves, the current fluctuations increased with increase in reduction potentials which is due to the gas evolution.

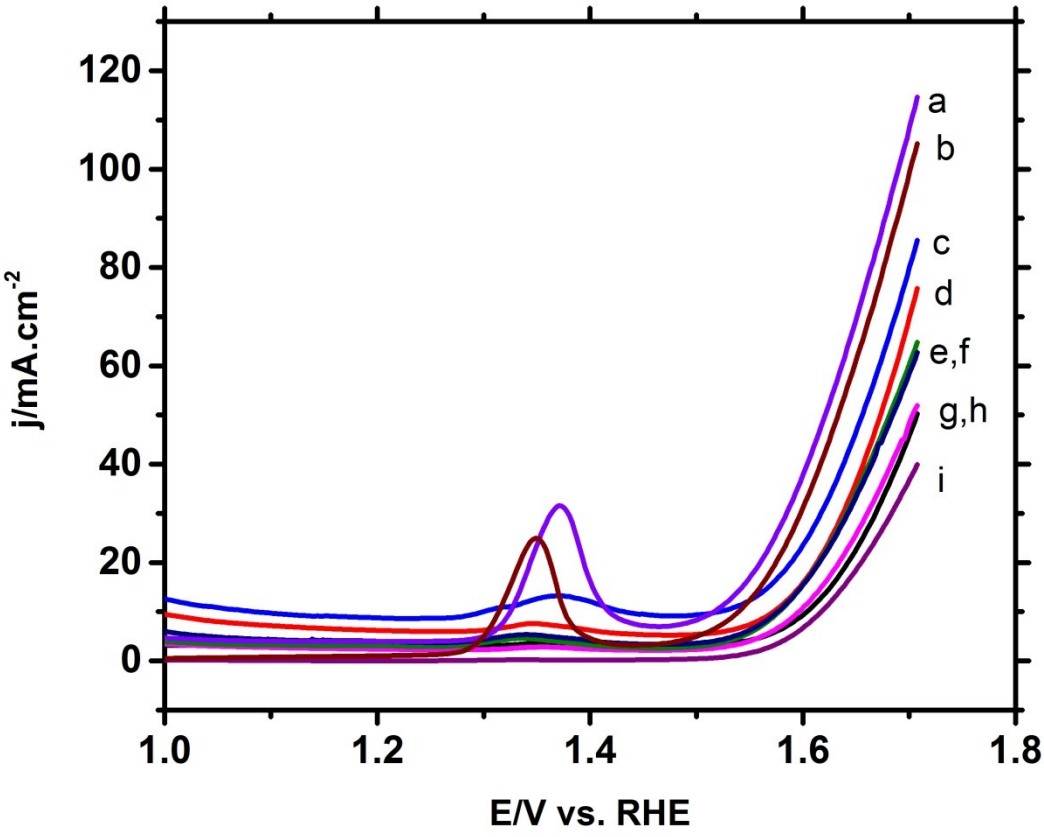


Fig. S3. OER performance of NiCo alloy electrodes prepared from different electrolytes

The best three electrodes a, b, c are corresponding to

1. **Potentiostatically deposited at – 1.4 V (0.05 M Co content)**
2. **Potentiostatically deposited at – 1.2 V (0.05 M Co content)**
3. **Galvanostatically deposited at – 10 mA/cm^2 (0.2 M Co content)**

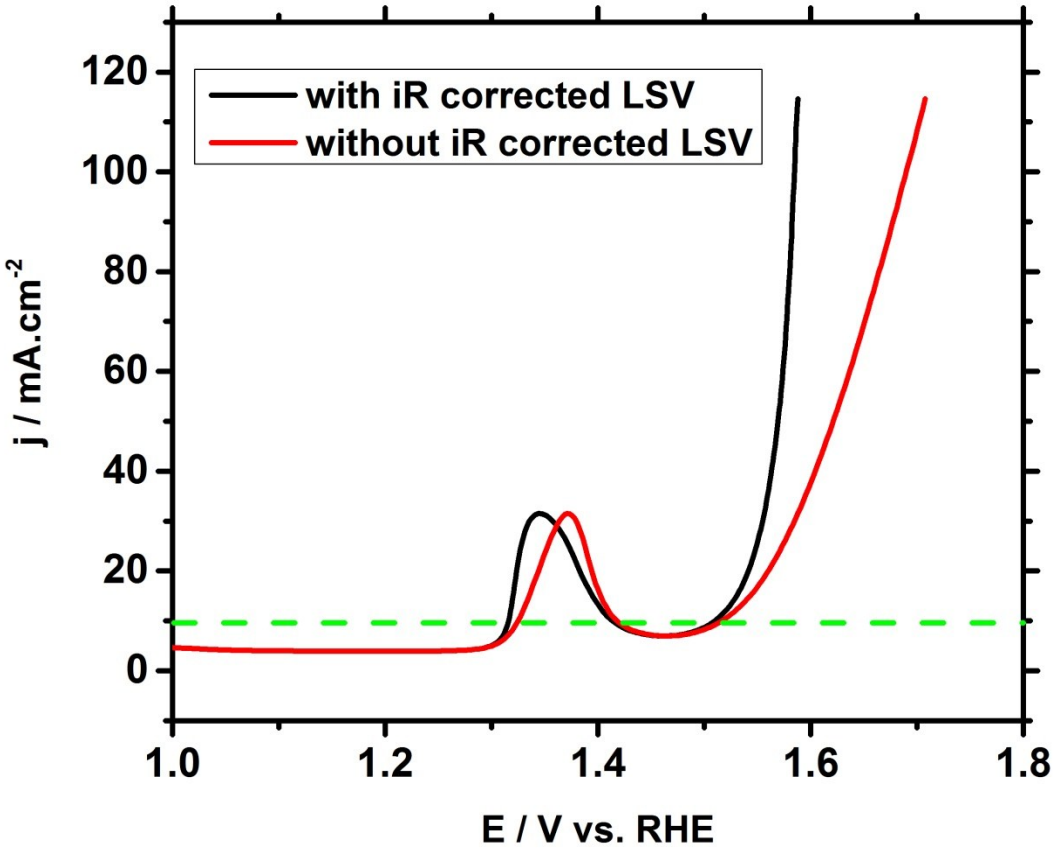


Fig. S4. Comparision of with and without iR corrected LSV of the porous NiCo alloy electrode

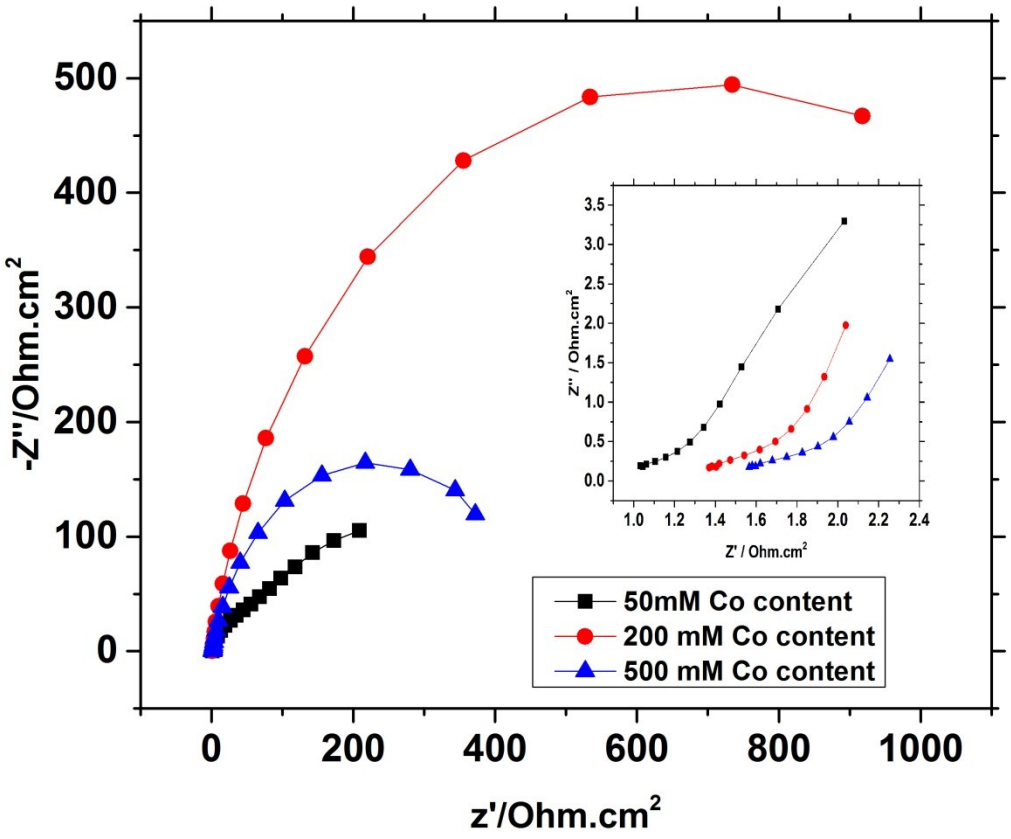


Fig. S5. Electrochemical Impedance Spectrum of best three OER performed electrodes (denoted as a, b, c in Fig S3)

Turn over frequency is calculated by this formulae.

$$TOF = jxA / 4Fm$$

j – Current density at overpotential

F - Faraday constant

A – Area of the working electrode

M – Mass of the active material

Reference: Nickel–vanadium monolayer double hydroxide for efficient electrochemical water oxidation. Nat. Commun. 7:11981 doi: 10.1038/ncomms11981 (2016).

Materials	η (mV)@ 10 mA/cm^2	Tafel slope (mV/dec)	TOF (S^{-1})	Ref
Ni-Co binary oxide layers	325	39	-	[S1]
NiCo- LDH	367	40	-	[S2]
$NiCo_2O_4$ NW-NiCo layered Oxide nanosheets	340	63	-	[S3]
Nickel-Cobalt oxide Hallow nano sponges	362	64.4	-	[S4]
Electrodeposited Hydroxide surface covered 3D-Porous NiCo alloy	307	63	0.002	This work

References:

[S1] M. Holzschuh, F. Simon and A. Eychmu, 2015, 2, 7851–7854.

[S2] H. Liang, F. Meng, M. Cab??n-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang and S. Jin, *Nano Lett.*, 2015, 15, 1421–1427.

[S3] J. Yin, P. Zhou, L. An, L. Huang, C. Shao, J. Wang, H. Liu and P. Xi, *Nanoscale*, 2016, 8, 1390–1400.

[S4] Y. Yang, H. Fei, G. Ruan, C. Xiang and J. M. Tour, 2014, 9518–9523.

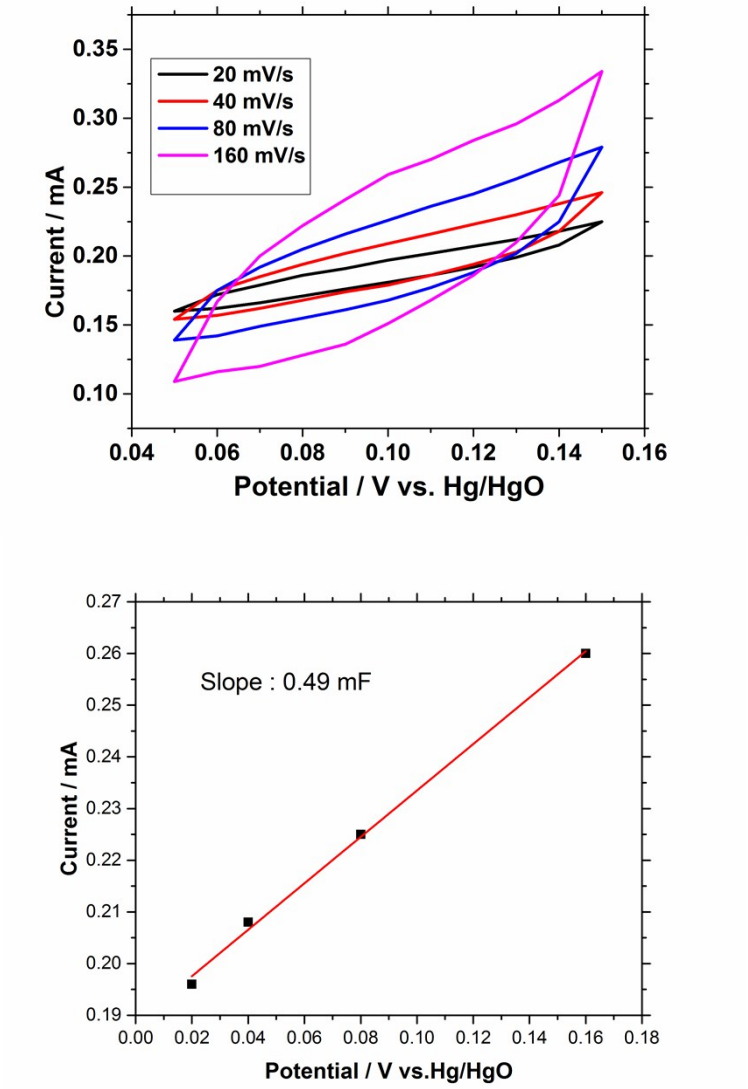


Fig. S6. CV@non-faradaic region for C_{dl} calculation

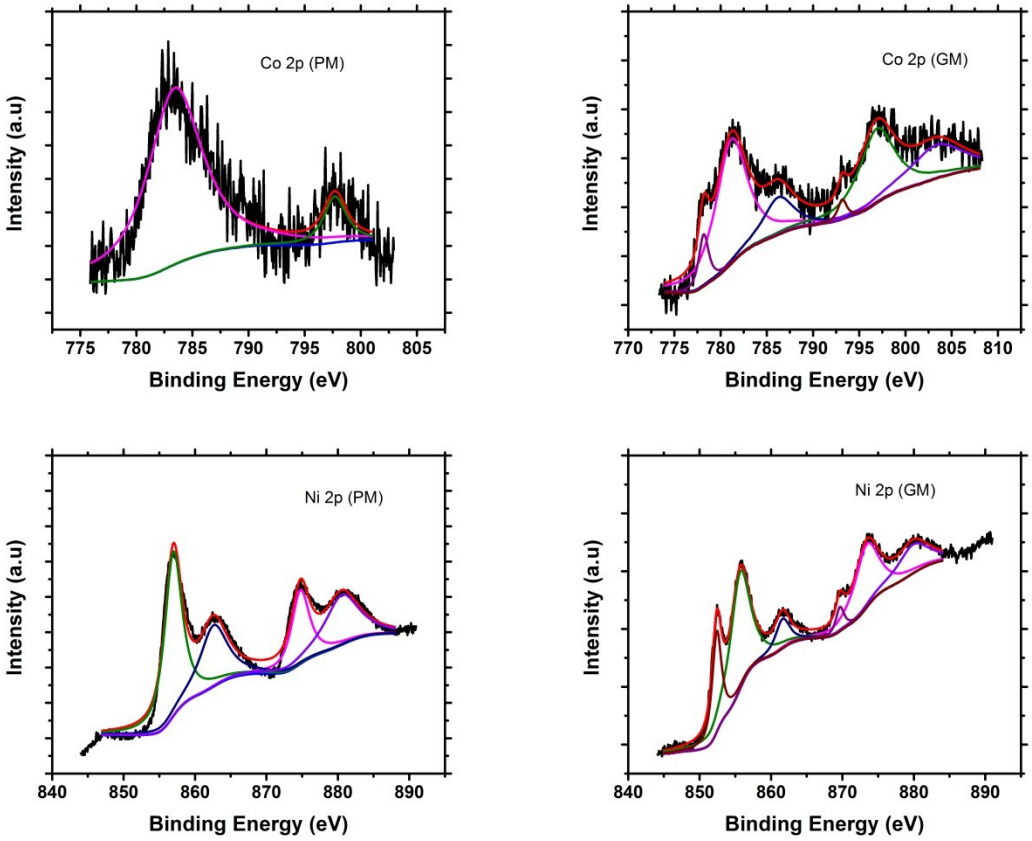
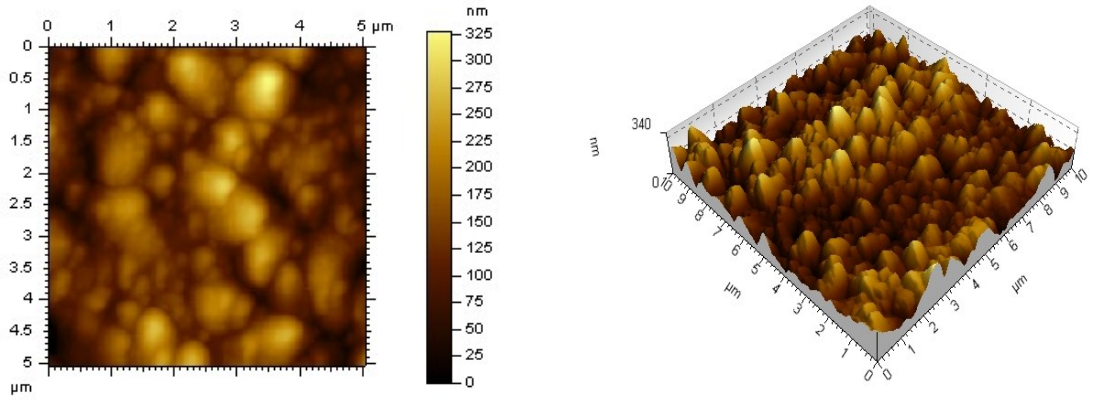


Fig. S7. XPS of NiCo alloys prepared by GM and PM modes.



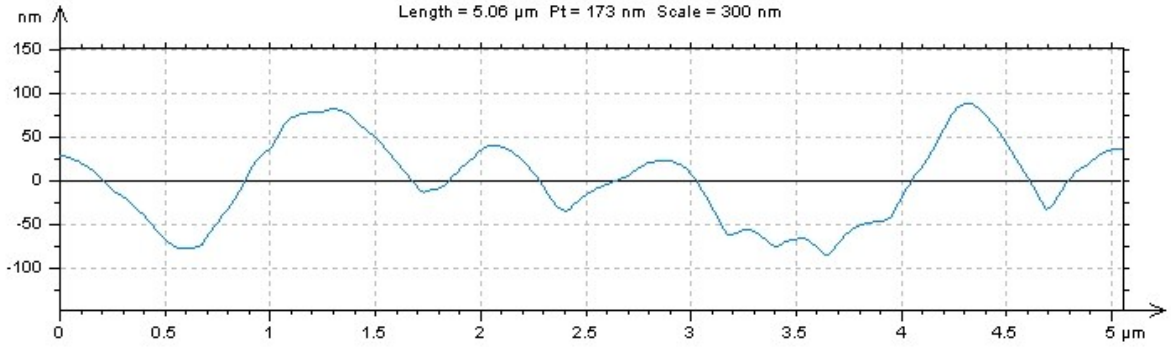


Fig. S8. AFM images (2D and 3D) and roughness profile of NiCo alloy deposited by galvanostatic method.

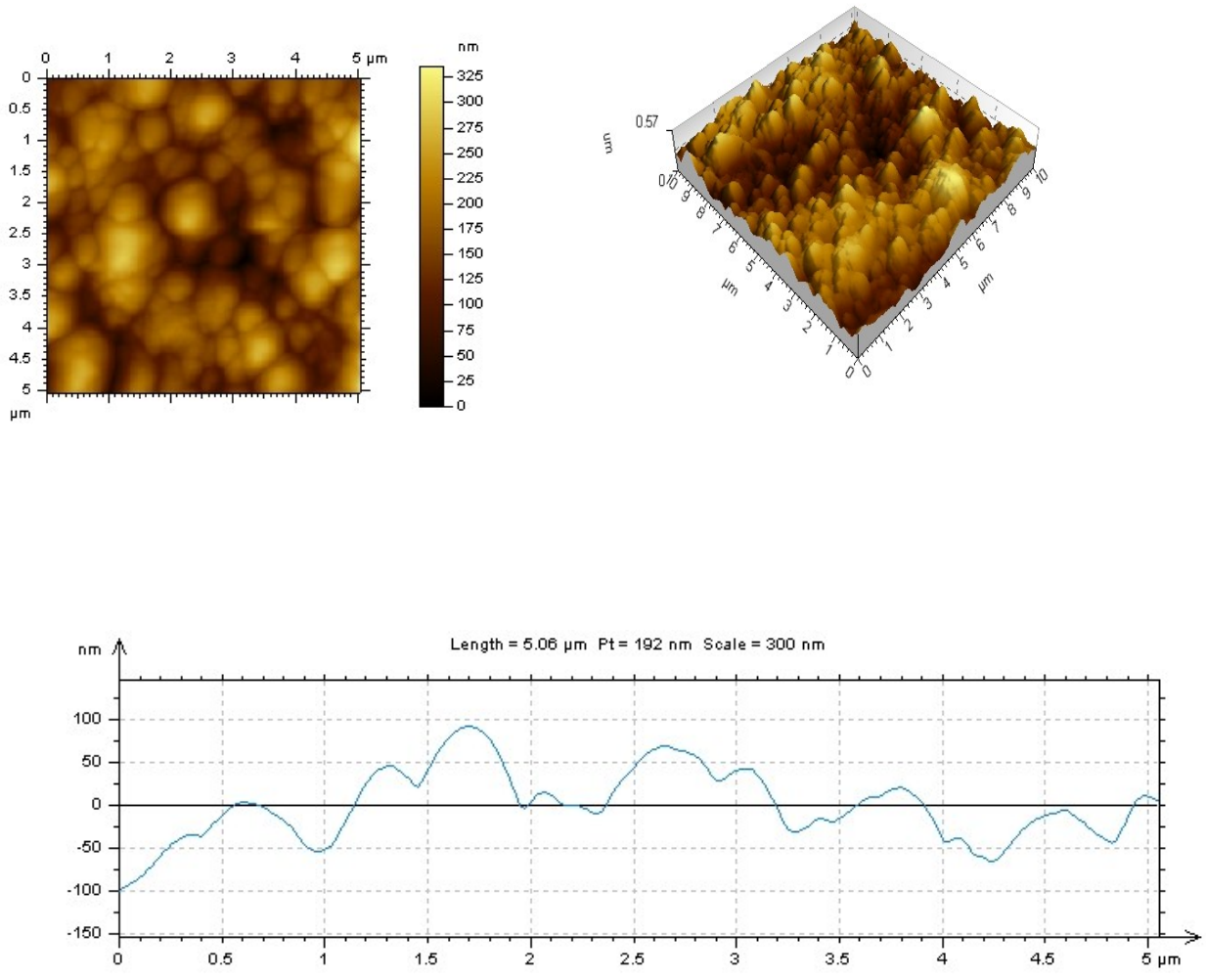


Fig. S9. AFM images (2D and 3D) and roughness profile of NiCo alloy deposited by potentiostatic method.

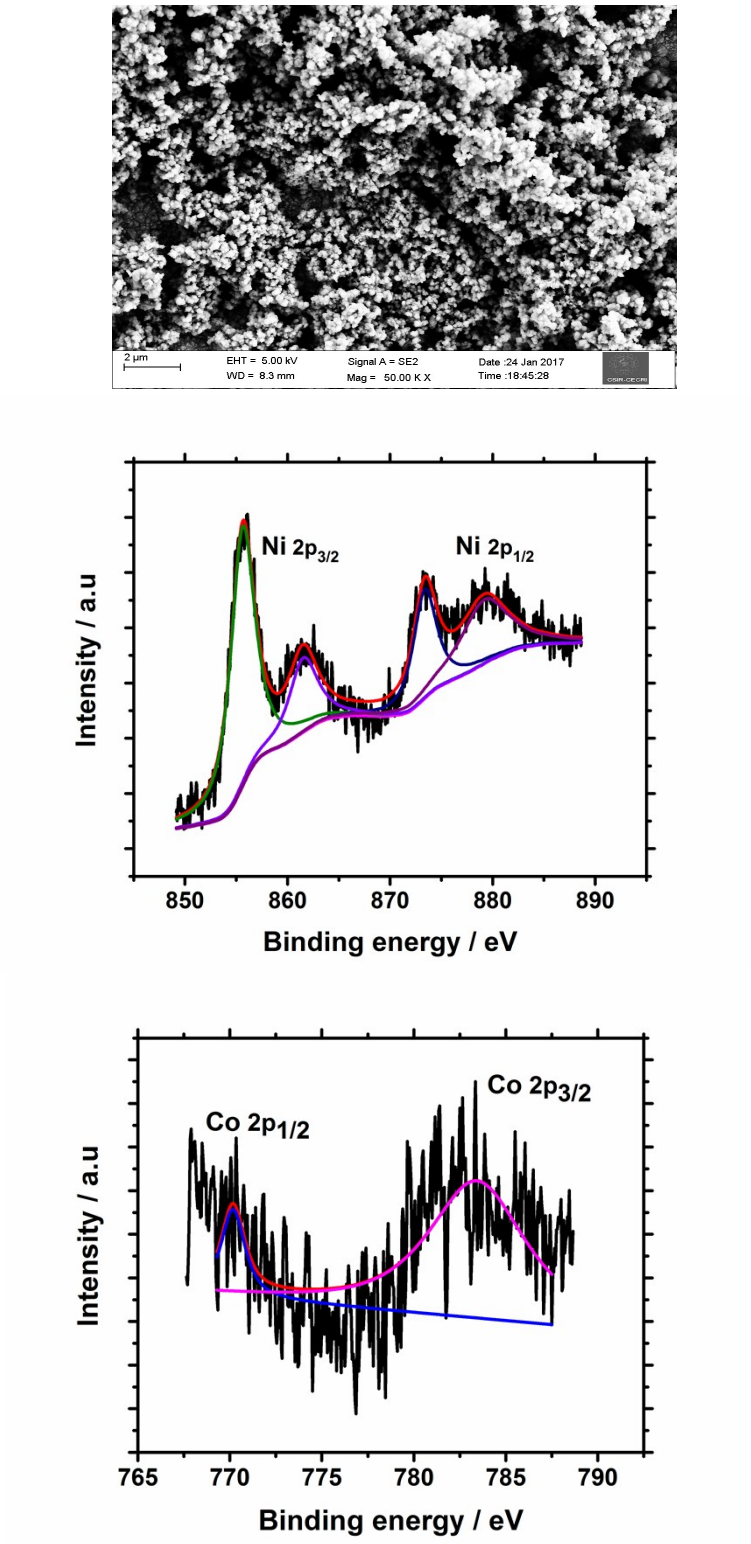


Fig. S10. SEM and XPS of porous NiCo alloy electrode after the electrolysis of 10 hours at 1.54 V vs. RHE