Binary metallic sponges as an efficient electrocatalyst for alkaline water electrolysis

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Abstract

Binary metallic sponges comprising of nickel–cobalt (NiCo) hydroxide/oxide composites are prepared using a simple pyrolysis method by employing cyanocobalamin as a new sacrificial template. Subsequently these highly porous materials are demonstrated as an efficient electrocatalyst for oxygen evolution reaction (OER) under alkaline conditions. Structure, morphology and porosity of these materials are controlled through thermal oxidation between 200 and 600 °C and the resultant materials are designated as NiCo-200, NiCo-400 and NiCo-600 respectively. Among the different materials studied in this work, NiCo-200 exhibits better electrocatalytic behaviour for OER with a lower overpotential of 420 mV for obtaining a current density of 10 mA/cm² along with a turnover frequency value of 0.0234 s^{−1}. The observed higher electrocatalytic activity is attributed to the presence of hydrophilic surface, enriched pores and crystalline nature of NiCo-200. Further the stability studies carried out under alkaline medium at a fixed current density of 20 mA/cm² showed that both NiCo-200 and NiCo-600 displayed a good stability and retain OER characteristics for a longer duration. Finally our results clearly show that the binary metallic hydroxide/oxide sponges could potentially act as a new class of electrocatalyst in energy conversion devices mainly for alkaline water electrolysis.

Graphic abstract Highly porous, binary Ni–Co metallic hydroxide/oxide sponges are prepared through a novel route using cyanocobalamin as a sacrificial bio-source. Structure, morphology and porosity of these metallic sponges are controlled by temperature. Further these cost-effective materials are explored as electrocatalysts for oxygen evolution reaction associated with alkaline water electrolysis.

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1 Introduction

Ever-growing demand for energy and power emphasizes mainly on the cost effective production of useful hydrogen fuel from water splitting so as to develop a clean energy. The depleting fossil fuels alarms for the uttermost importance to seek alternative energy sources. Electrochemical method of water splitting provides a cheapest and environmentally benign route for the production of hydrogen and oxygen. Iridium oxide (IrO_2) and ruthenium oxide (RuO_2) are the renowned electrocatalysts employed for oxygen evolution reaction (OER); but it lacks commercialization because of its scarcity, high cost and instability under the harsh conditions thereby preventing a long term usage for OER applications [1]. To overcome these issues, earth abundant first row transition metals received special concern since the properties of oxides/hydroxides of these metals are tuneable for obtaining a better catalytic activity in terms of lower overpotential, higher catalytic current and superior stability etc. [2, 3]. In order to enhance the electrocatalytic activity of transition metal hydroxides/oxides, many essential characteristics like intrinsic electronic conductivity, defective states (like oxygen vacancies), crystalline facets, surface functional groups for hydrophilicity, surface area, composition, morphology, redox property and particle size are to be introduced and could also be modulated [4–7]. Among these, the morphology and facets are interdependent and several heterostructures exposing specific facets are prepared by optimising the reaction conditions and concentration of the reactants [8]. Even then only a little control at defective sites can be introduced in metal oxides mostly through annealing at high temperature in a harsh reducing environment [9]. In order to address the poor conductivity of metal oxides, conductive carbon supports (acetylene black, graphene, multi-walled carbon nanotubes [MWCNTs] etc.) and metallic nanostructures are added for obtaining better electrocatalytic performance [10].

Three dimensional mesoporous structures of metal oxides are known to expose higher number of active sites and it is widely used as an electrocatalyst for sensors, supercapacitors and water splitting applications [11–13]. Various templates assisted and surface etching methods are followed for the preparation of such porous structures. Among them one of the simple methods for preparing 3D porous materials is nano-casting method in which carbon (soft template) and silica (hard template) are used as the templates [14]. Carbonisation of metal organic frameworks (MOF) is one of the nano-casting methods where the coordinated macrocyclic carbon containing ligand acts as the

soft template. During the carbonisation of MOF, the in situ production of gaseous bubbles is responsible for the formation of pores. While using this method, there are certain requirements for pore formation viz., (i) the gas bubbles should be stable, (ii) the carbon precursor should have a hydrophilic (to enhance the solubility of the molecule) and a hydrophobic group (stabilizes the bubbles) and (iii) optimization of solvent removal temperature which is crucial for determining the resultant structure [15, 16]. Recently, Ding et al. [17] used iron chloride hexahydrate, tri-sodium citrate, polyvinylpyrrolidone, glucose and sodium carbonate as the precursors and stabilizing agents for the preparation of hierarchically porous $\text{Fe}_3\text{O}_4/\text{C}$ nanocomposite microspheres. Here CO_2 gas evolved as a result of carbonization of organic precursors and the resultant carbon coating was formed by the self assembly of hydrophobic layer around it. Chen et al. [18] used nitrate precursor of zirconium for the preparation of porous ZrO_2 where the evolved NO_2 gas acts as a soft template. Here there is no carbon precursor added and the NO_2 gas is liberated from nitrate salt. The major limitations of using MOF for synthesizing OER catalysts are cumbersome and tiresome preparation strategy involving multiple steps and their characterisation [19].

Some of the naturally existing coordination compounds structurally resemble MOF and the replacement of MOF by these compounds eliminates the MOF synthesis step. In literature, Mironova-Ulmane et al. [20] used cellulose as a bio-template instead of synthetic polymers/MOFs for the preparation of nickel oxide. Rath et al. [21] synthesized NiO based composite using egg shell membrane as a template. Huang et al. [22] used pyrolyzed iron-folic acid composite for oxygen reduction reaction (ORR) and found that the enhanced ORR activity is due to polyaromatic hydrocarbons, quaternary-type (graphitic) nitrogen and their coordinated structure. Zhang et al. [23] employed Co_3O_4 decorated blood powder derived heteroatom doped porous carbon as a bifunctional electrocatalyst for oxygen evolution and reduction reactions (OER and ORR). From these studies, it is evident that bio-compounds with a core metal atom and a large organic macrocycles on pyrolysis favour the successful design and formation of 3D porous structures. The final product encompasses the synergy of metal oxide/hydroxide and the residual carbon groups that introduce desirable structure and morphology along with intrinsic characteristics for exhibiting better electrocatalytic activity.

In this work, we have proposed a simple pyrolysis method for the preparation of highly porous oxides/hydroxides of binary metals using cyanocobalamin (CB)

as a sacrificial template (Scheme 1). CB is a biologically existing cobalt complex having a macrocyclic structure composed of carbon network containing various functional groups. This carbon containing macrocycle acts as a soft template for pore formation through emanating gaseous byproducts. As-prepared binary metallic hydroxides/oxides materials composed of nickel and cobalt possess higher porosity mostly of mesoporous nature and they are used as an electrocatalyst for oxygen evolution reaction in alkaline medium. The synergy of Ni and Co based oxides is known to improve the OER kinetics which arises due to the change in local electronic environment [24, 25].

2 Experimental section

2.1 Chemicals

The list of chemicals/materials used and the respective companies from where they are procured are given as follows: Cyanocobalamin (Himedia Laboratories, Mumbai, India), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, Bangalore, India), Nafion (Sigma Aldrich, Bangalore, India) and Isopropanol (Sigma Aldrich, Bangalore, India). Millipore water obtained from Milli-Q system having a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was used for all the experiments. Graphite rods of length (150 mm) and radius (3 mm) were procured from Sigma Aldrich, Bangalore, India.

2.2 Preparation of binary metal hydroxide/oxide sponges

NiCo binary metallic sponges or foams were prepared by a simple pyrolysis method. About 36 mg of CB and 183 mg of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL of water to form an uniform dispersion and then heated to evaporation at 80°C in presence of air. The precipitate thus obtained was

Scheme 1 Schematic representation of the preparation of NiCo composites at different annealing temperatures

annealed at different temperatures viz., 200, 400 and 600°C respectively for 4 h in air atmosphere and the resultant materials were labelled as NiCo-200, NiCo-400 and NiCo-600 respectively. The pyrolyzed products thus obtained were used as such for electrocatalytic studies without any further treatment. For comparing the role of each of these precursors in the product (sponge) formation and their respective electrocatalytic activity, nickel nitrate alone was subjected to thermal treatment at the same temperatures of 200°C and 600°C and the resultant products are marked as Ni-200 and Ni-600 respectively.

2.3 Electrode preparation for electrochemical studies

The graphite rod was polished well in emery sheets of different grades such as 6/0, 3/0 and 2/0 to obtain a mirror like surface before modification [26]. In order to study OER electrocatalytic activity, the pre-cleaned graphite rod was modified using a catalytic ink prepared with the resultant materials. For the modification of working electrode, a catalytic ink was prepared using the following procedure: About 5 mg of NiCo-X°C ($X = 200, 400, 600$) was dissolved in 1 mL of water–isopropanol mixture (1:1 v/v ratio) along with 40 μL of Nafion added as a binder. It was then ultrasonicated to obtain a homogeneous dispersion and the ink thus obtained was drop-casted (10 μL) over the polished graphite electrode and dried. Further these electrodes were employed for the electrochemical studies. The catalyst loading on the graphite electrode was calculated to be $0.71 \text{ mg}/\text{cm}^2$. The electrochemical studies were carried out by a computer controlled Biologic instrument model SP-240 provided with EC Lab software procured from France.

Electrochemical studies for the investigation of oxygen evolution reaction characteristics were carried out using a three electrode setup where the active material loaded onto graphite electrode was used as a working electrode, saturated calomel electrode (SCE) as the reference electrode and platinum coil having high surface area was used as the counter electrode respectively. An aqueous solution of 1 M KOH was employed as the electrolyte and linear sweep voltammetry was used for the study by recording the corresponding voltammograms between the potential range from 0 to 1 V at a fixed scan rate of 5 mV/s. In this work, all the electrochemical studies associated with OER are performed using saturated calomel electrode (SCE) as a reference electrode. The potential values are experimentally measured using this reference electrode and later on these potential values are converted to reference hydrogen electrode (RHE) using the following Nernst equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \times \text{pH} + E_{\text{SCE}}^0$ where E_{RHE} is the final converted potential with respect to RHE, E_{SCE} is the measured

potential against SCE and E_{SCE}^0 is the standard electrode potential of saturated calomel electrode (0.241 V). Finally the electrocatalytic activity of various composites was compared at two different current densities (10 mA/cm² and 20 mA/cm²) and potential values (400 mV and 500 mV) in order to evaluate and compare the characteristics of electrocatalytic parameters.

2.4 Instrumentation

Surface morphology of the resultant materials was observed through scanning electron microscopy (SEM; Vega-3 TESCAN) and field emission scanning electron microscopy (FESEM; Hitachi model S3000-H). Micro-structural characteristics were analyzed by using transmission electron microscopy (TEM; FEI Technai 20 G² model) and high resolution transmission electron microscopy (HRTEM; FEI Technai F20 Super-Twin model). XRD studies were carried out using Cu K α radiation as a source of X-ray having a wavelength of 1.540 Å using XPERT-PRO multipurpose X-ray diffractometer procured from The Netherlands. Raman studies were performed by using Reinshaw in Via Raman microscope using wire 2.0 version software. Similarly FTIR spectra were recorded by using Bruker Optik GmbH spectrometer. The pore volume, pore number and surface area values were determined from Quantachrome® ASiQwin™ Brunett–Emmett–Teller (BET) analyzer. Moreover XPS analysis was performed using Thermo Scientific equipment, Multilab-2000 model obtained from UK. Finally, Thermogravimetric analysis (TGA) analysis was carried out in air atmosphere using an instrument, SDT Q600 V8.3 Build 101 model.

3 Results and discussion

3.1 Structural and morphological analysis

Various NiCo composites possessing unique cellular arrangement are prepared by a simple pyrolysis method using CB as an efficient pore creating gaseous source thus

acting as a soft template. The hydrophilic and hydrophobic groups present in the corrin ring of macrocyclic CB serve to stabilize the gaseous by-products and helps in directing the formation of porous structure. The pre-treatment of the reactants is carried out at 80 °C for evaporation of solvent resulting in the formation of reddish swollen mass [Electronic supplementary information (ESI); Fig. S1]. The dry mass was then heated at different temperatures (200, 400 and 600 °C) to obtain the porous structured materials. Annealing of these samples is examined at two different rates of temperature rise viz., 1 °C/s and 5 °C/s. The former resulted in a swollen mass while higher heating rate resulted in charring of the sample (data not shown). Initial assessment of porosity is done from the swollen structure of NiCo composites compared to the product obtained from metal precursor alone that are also pyrolyzed under the same condition. From the photographic image (Fig. 1), the three NiCo composites namely NiCo-200 (B), NiCo-400 (C) and NiCo-600 (D) seems light weight, puffy and possess numerous air racks that can be visibly predictable whereas Ni-200 (A) and Ni-600 (E) exist in the powder form. The average density values of these NiCo composites (viz. 200, 400 and 600 °C) are found to be 66.18, 21.47 and 49.59 mg/cm³ respectively.

In order to confirm the porosity and to obtain the insights about the structure and morphology, SEM and TEM analyses were carried out for the as-prepared NiCo samples. SEM images show that the composite materials display foam like appearance and possess several voids compared to the control samples viz., Ni-200 (A) and Ni-600 (E) [ESI; Fig. S2]. NiCo composites alone have the spongy pockets with large internal volume whereas Ni-200 and Ni-600 exhibit the formation of homogeneous particles. In spite of larger racks, NiCo-200 (B) has thick walls while that of NiCo-400 (C) and NiCo-600 (D) are relatively thin [ESI; Fig. S2]. It is evident from these SEM images that it is due to the peculiar dense arrangement of porous leaf like structures.

FESEM images shown in Fig. 2 clearly display the formation of thick walls for NiCo-200 (A) and the platelet-like building blocks of the thick walls which are approximately

Fig. 1 Photographs showing the difference in physical appearance and the colours of nickel–cobalt binary composites and the starting materials individually subjected to heat treatment namely, **A**

Ni-200, **B** NiCo-200, **C** NiCo-400, **D** NiCo-600, **E** Ni-600 and **F** CB-600 respectively

Fig. 2 FESEM and TEM images of NiCo-200 (**A**, **D**), NiCo-400 (**B**, **E**) and NiCo-600 (**C**, **F**) showing the nanoporous nature and the variation in porous arrangement of these materials

1 μm in length. These platelets are in aggregated form but arranged in a unique fashion by creating larger voids. A small platelet of NiCo-200 (Fig. 2D) is analysed using TEM to have a closer view of the platelet surface at a higher resolution. TEM image depicts that the surface is thick, coarse and the pores are uniformly distributed over the surface. This unique assembly of platelets creates a large number of interstitial spaces and different dimensions of porosity are seen. Such an arrangement is essential and useful in electrochemical studies for the maximum utilization of active sites and also for electrolyte diffusion.

Annealing at different temperatures will alter the morphology of the resultant materials. Hence, the pre-treated samples further on heating at 400 $^{\circ}\text{C}$ (Fig. 2B) shows distinctly arranged pores that are different from NiCo-200 which may be probably due to the difference in rate of release of gaseous by-products. NiCo-400 possesses a spongy texture and high transparency in imaging indicating the presence of multiple pores. A non-spongy fine layer is also seen on the surface. The porosity in case of NiCo-600 (Fig. 2C) is more suitable to be called as nanoporous cellular structure rather than mere a spongy material. It has a periodically arranged interconnected cellular structure with well-defined porosity and ordered pores. The diameter of these pores is of few nanometers and clearly

of open cellular type. TEM image shown in Fig. 2F depicts the presence of fine nanopores in case of NiCo-600.

HRTEM assisted selected area electron diffraction (SAED) analysis is carried out for obtaining the particulars of lattice arrangement. Figure 3 shows the HRTEM images obtained for different binary NiCo composites used in this study and their corresponding SAED patterns are displayed as insets. HRTEM images show the structure of lattice fringes at atomic level resolution from which the “*d*” spacing value is determined which coincides with the standard JCPDS “*d*” space value of the corresponding composites. Similar lattice spacing information was also calculated from SAED pattern and found to be in agreement with standard values [ESI; Tables S1, S2, S3]. Regarding the crystal structure, NiCo-200 exhibits a combination of crystalline and amorphous areas and the corresponding SAED pattern recorded in both the areas clearly distinguishes them. The fringed region is purely single crystalline in case of NiCo-200 whereas NiCo-400 and NiCo-600 exhibit a polycrystalline arrangement.

Further the physical parameters of as-prepared samples including the type of porosity, surface area and pore volume were determined by recording the N_2 adsorption–desorption isotherms [ESI; Fig. S3] and the corresponding values are shown in Table 1. From these isotherm profiles, it is obvious that all the samples exhibit

Fig. 3 HRTEM images of **A** NiCo-200, **B** NiCo-400 and **C** NiCo-600 respectively showing the formation of lattice fringes and their corresponding SAED pattern are shown as insets

Table 1 BET surface area values along with the pore size and pore volume measured for the different binary NiCo composites and for the control samples

Sample	BET surface area (m ² g ⁻¹)	Pore size (nm)	Pore volume (cm ³ g ⁻¹)
Ni-200	0.04	56.85	0.000590
NiCo-200	10.62	21.21	0.056293
NiCo-400	124.71	6.16	0.192104
NiCo-600	41.91	15.40	0.161380
Ni-600	2.72	13.86	0.009437

Type IV isotherm as per the IUPAC norms. The hysteresis loops of NiCo-400 and NiCo-600 ranges between 0.6 and 1.0 P/P₀ indicating the presence of mesopores whereas for NiCo-200, Ni-600 and Ni-200 the values range between 0.8 and 1.0 P/P₀ indicating predominantly the formation of macropores [27, 28]. From BJH (Barrett, Joyner and Halenda) plots [ESI; Fig. S4], it is understood that there is a bi-modal pore size distribution of the pores comprising of the mesoporous and macroporous type of porosity except for the case of NiCo-400 that possesses the porosity associated with the microporous and mesoporous types.

3.2 Compositional analysis of binary NiCo metallic sponges

Crystal structure, phase purity and chemical constituents of the porous, binary NiCo composites are investigated using XRD analysis. Typical XRD patterns of the calcinated products obtained at 200 °C (both Ni and NiCo) are shown in Fig. 4a and b. In case of Ni-200, the appearance of peaks at 12.7°, 25.6°, 32.9°, 33.9°, 36.4°, 43.7° and 59.03°

Fig. 4 XRD patterns of **a** Ni-200, **b** NiCo-200, **c** NiCo-400, **d** NiCo-600 and **e** Ni 600 respectively

indicates the formation of nickel oxyhydroxide (JCPDS No.: 00-006-0075). The broad FWHM shows that NiCo-200 is crystalline and exhibits major peaks at 12.8°, 25.6° and 33.1° corresponding to nickel oxyhydroxide phase [29, 30]. The peak at 24.2° indicates the presence of carbon components in NiCo-200 [31]. Similarly, NiCo-400, NiCo-600 and Ni-600 exhibit peaks at 37.18°, 43.3°, 62.9°, 75.54° and 79.55° ascribed to (111), (200), (220), (311) and (222) planes of NiO respectively (JCPDS No.: 01-073-1519) [32]. No obvious peaks associated with cobalt and its oxides

form are observed in XRD analysis. This may be due to the fact that Ni^{2+} and Co^{2+} have same atomic radii and their corresponding oxide peaks fall in the same region in XRD spectra as well as due to the lower amount of Co present in the resultant materials [33]. Moreover, XRF studies show the ratio of Co content to its nickel counterpart is 1:38 that will be discussed later. The average particle size is calculated from XRD using Debye–Scherer equation shown below [34].

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite size in nm, λ is the wavelength of radiation (Cu is the radiation source used and the wavelength is 1.543 Å), β is full-width at half maximum (FWHM) value in radians and θ is the diffraction angle respectively. The average crystallite size values are estimated to be 12.2, 6.95, 9.74, 19.23 and 28.18 nm respectively for Ni-200, NiCo-200, NiCo-400, NiCo-600 and Ni-600.

Although smaller particle size is expected to increase the surface area, there are several factors contributing to the overall surface area of the sample. Since these particles are in aggregated form, most of the area will not be exposed for ion adsorption from the electrolyte. Hence it is the shape and morphology of the particle that mainly determine the surface area which depends partly on the particle size. Besides this, the electrochemical surface area differs from the geometrical surface area where the former mainly depends on the presence of catalytic sites like facets, oxygen deficient centres and hydrophilic or hydrophobic groups [6, 33].

The distribution of Ni and Co ions in the binary NiCo composites is analyzed using XRF mapping and the approximate ratio of Ni and Co is calculated to be 36–38:1 [ESI; Fig. S5 and Table S4]. This is consistent with the molar ratio (38:1) of Ni^{2+} and Co^{2+} taken initially during the preparation and it is also coherent with the absence of Co oxide peaks noted in the XRD studies.

The chemical composition and surface oxidation states of the binary composites are investigated further using XPS studies and the corresponding spectra are shown in Fig. 5. The various peaks observed in the deconvoluted spectra of Ni 2p are tabulated in ESI; Tables S5, S6 and S7. Nickel exists as Ni^{3+} ion as evidenced by the $2p_{3/2}$ peak observed at 856.6 eV and $2p_{1/2}$ peak at 874.2 eV in NiCo-200 corresponds to the formation of oxyhydroxide [35, 36]. In case of NiCo-400, the doublets of $2p_{3/2}$ are located at 853.9 and 855.7 eV and $2p_{1/2}$ at 871.6 and 873.0 eV respectively. Similarly for NiCo-600, the $2p_{3/2}$ peaks are observed at 853.8 and 855.9 eV and $2p_{1/2}$ at 871.2 and 873.0 eV respectively. The binding energy values of ~854 eV and

871.8 eV corresponds to Ni^{2+} ions in octahedral site and the peaks around 855.7 and 873.4 eV corresponds to Ni^{3+} ions in tetrahedral sites. This indicates that Ni exist as +2 and +3 oxidation states in NiO. Higher oxidation state (+3) is formed on NiO surface in order to maintain the electrical neutrality [37, 38]. These values clearly indicate that Ni is in +3 oxidation state for NiCo-200 in contrast to NiCo-400 and NiCo-600 where Ni predominantly exists in +3 oxidation state. Further the presence of peaks at 780.6 eV ($2p_{3/2}$) and 795.8 eV ($2p_{1/2}$) indicates the presence of cobalt as Co^{2+} in case of NiCo-200. Similarly the appearance of peaks at 779.9 (Co $2p_{3/2}$), 796.0 (Co $2p_{1/2}$) and 780.7 (Co $2p_{3/2}$), 796.4 (Co $2p_{1/2}$) confirm the presence of Co in +2 oxidation state for NiCo-400 and NiCo-600 respectively. Overall the peaks corresponding to Co indicate the existence of +2 oxidation state for Co in all the three NiCo composites [39, 40]. In addition, XPS spectra also show the formation of satellite peaks corresponding to both Ni and Co confirming the presence of these elements in all the composites. On comparing C 1s spectrum of these three composites, the carbon content has significantly decreased for NiCo-400 and NiCo-600 as shown in Fig. 5B & C than NiCo-200 (Fig. 5A) indicating that carbon particles are removed during thermal decomposition carried out at higher temperature. Moreover, in case of O 1s spectrum both NiCo-400 and NiCo-600 composites show depletion in hydroxyl groups while the intensity of M–O–M peak is considerably increased compared to NiCo-200 [41]. The presence of N in different NiCo composites are confirmed from the peak positions noted at 398–410 eV. Among the different samples, NiCo-200 showed < 1% of pyridinic nitrogen, which is known to enhance the oxygen evolution activity. The carbon atom adjacent to pyridinic nitrogen provides an active site for the adsorption of OH^- ions and hence influences OER activity. Further NiCo-400 and NiCo-600 showed a very less N content as evident from the formation of a feeble N peak in XPS. Finally the phosphate group is also not disintegrated as identified by the formation of peaks at 132–134 eV in the XPS spectrum of NiCo composites [42, 43].

From FTIR spectral analysis, it is evident that NiCo-200 is decorated with a C=O or H–O–H (1631 cm^{-1}) and C–N (1567 cm^{-1}) functionalities and the intensity of these groups are decreased with rise in temperature [ESI; Fig. S6]. The peak at 1360 cm^{-1} corresponds to N–O stretching vibration arising from the nitrate ion. The region between 1201 and 400 cm^{-1} corresponds to M–O bond vibration. The high intense peak noted at 1049 cm^{-1} seen in case of NiCo-400 and NiCo-600 is due to the adsorbed oxygen present in NiO [39, 44]. From XPS and FTIR spectral analyses it is evident that the hydrophilic groups like C–O and O–H are enriched in case of NiCo-200 than in the remaining composites. Such hydrophilic groups help in

◀**Fig. 5** XPS spectra obtained for various binary NiCo composites such as **A** NiCo-200, **B** NiCo-400 and **C** NiCo-600 respectively. The labels for the corresponding elemental peaks are given in the left side of the figure

the adsorption of hydroxide ions on the surface which is the initial step for oxygen evolution reaction in alkaline medium.

3.3 Elucidation of mechanism behind porous structure formation

During the initial pre-treatment (at 80 °C) itself, it is noted that a reddish and slightly swollen mass is formed [ESI; Fig. S1]. Hence the origin of porosity starts from the pre-treatment step itself. Thermogravimetric analysis (TGA) on the pre-treated sample shown that the weight loss change starts gradually at 60 °C [ESI; Fig. S7] [23]. When the temperature is raised to 200 °C, a significant weight loss occurs by 29.57%. The weight loss occurs before 200 °C is predominantly due to carbon constituents from CB and water molecules from Ni precursor which results in creating the architecture of pores. At 200 °C, there is only partial decomposition occurs and most of the functional groups are still present in the composite. This is evidenced from XPS and FTIR studies indicating the presence of carbon, nitrogen and oxygen moieties like C–O, O–H, C–N and C–H groups. A sudden drop of weight loss of 49.51% occurs between the region 200–400 °C which results in further introduction of high porosity in case of NiCo-400. The possible evolving gases known to introduce porosity are $\text{NH}_{3(g)}$, $\text{NO}_{2(g)}$, $\text{CO}_{2(g)}$ and $\text{H}_2\text{O}_{(g)}$ formed by the disintegration of surface functional groups like –CONH₂ and –OH present in the corrin ring of CB. Liu et al. [45] proposed that NH₃ plays a key role in the controlled precipitation of metal ions as $\text{M}(\text{OH})_n$ or MOOH which in turn influence the overall morphology. But the role of phosphate is not known and we assume that there is a possibility of surfactant like molecule formation within the dough taking into account of its shape directing property. While reaching 600 °C, the weight loss is negligible (0.76%) and the composition remains same as NiO. But there is a difference in the pore shape and morphology of the final resultant NiCo-600 composite. To conclude, the emanation of pores is due to the evolution of gaseous by-products and the particle rearrangement during annealing.

The possible mechanism involved in the formation of porous metallic sponges is proposed below [45].

3.4 Binary NiCo metallic sponges as electrocatalysts for OER

The electrocatalytic activity of as-prepared, porous, binary NiCo composite materials towards OER is investigated. These studies are performed using linear sweep voltammetry (LSV) studies in 1 M KOH aqueous solution at a fixed scan rate of 5 mV/s and the corresponding LSV curves are shown in Fig. 6A. These experiments were carried out without the addition of any conducting carbon to NiCo composites. The overpotential required to obtain a constant current density of 10 mA/cm² (as per recent benchmark scale this current density is equal to minimum required efficiency for solar to energy conversion) is measured to be 420 mV for NiCo-200 while for Ni-200 it is calculated to be 440 mV. Under identical condition, the state-of-art OER catalyst, IrO₂ requires overpotential of 294 mV to obtain 10 mA/cm² current density. These results are closer to the reports of NiOOH reported by Kim et al. and IrO₂ by Maruthapandian et al. [46, 47]. For comparison similar studies were also carried out with bare graphite rod electrode without the coating of any catalyst. This particular electrode displays overpotential of 680 mV to obtain 10 mA/cm² current density, which is very much higher than the binary metallic systems. Even though at 10 mA/cm², both NiCo-200 and Ni-200 shows only a difference of 20 mV in overpotential, at higher current densities the catalytic activity of NiCo-200 is found to be much higher. At $j = 20 \text{ mA/cm}^2$, the overpotential values exhibited by NiCo-200 and Ni-200 are found to be 480 mV and 530 mV respectively.

These LSV curves exhibit a sharp redox peak between the potential range of 1.38–1.51 V versus RHE which is due to the formation of MOOH (M = Ni or Co) intermediate [ESI; Fig. S8]. The charge under this voltammetric peak is relatively higher for NiCo-200 ($1.22 \times 10^6 \text{ mC/cm}^2 \text{ mg}$) than Ni-200 ($0.85 \times 10^6 \text{ mC/cm}^2 \text{ mg}$) indicates the presence of larger number of electro-active sites (Fig. 6A and Table 2). This indicates that apart from composition, there are additional factors that will also influence the OER activity. The presence of pyridine moiety as evidenced from XPS spectra provides an electropositive

Fig. 6 **A** Linear sweep voltammograms displaying OER characteristics associated with different binary NiCo composite materials namely (a) IrO₂, (b) NiCo-200, (c) Ni-200, (d) NiCo-600, (e) NiCo-400, (f) Ni-600 and (g) bare graphite rod respectively in 1 M KOH aqueous solution at a scan rate of 5 mV/s. **B** Bar diagram comparing the electrocatalytic OER behaviour of as-prepared materials at two

different overpotential values namely 400 mV and 500 mV. **C** Tafel plots of (a) IrO₂, (b) NiCo-200, (c) NiCo-400, (d) NiCo-600, (e) Ni-200, (f) Ni-600 and (g) bare graphite rod respectively. **D** Stability curves of (a) NiCo-200 and (b) NiCo-600 performed for the duration of about 48 h at an applied potential of 1.71 V and 1.78 V versus RHE respectively

carbon centre for OH⁻ adsorption and the presence of hydroxyl groups offers hydrophilicity to the interface thereby enabling the effective adsorption of OH⁻ ions from the electrolyte [5, 48]. The role of cobalt ions in binary metal oxide composites for OER reaction is a controversial one. Previous reports show that it enables a volcano like activity and at certain atomic weight percentage of Co²⁺ the OER activity will be decreased. A lower amount of Co doping (< 3 atomic weight %) to Ni²⁺ will also influence the OER activity by assisting in the formation of Ni³⁺ intermediate [49, 50]. Here we have taken equal concentration of CB and hence equal concentration of cobalt ions for the preparation of binary NiCo composites. Figure 6B showed the comparative results

of OER catalytic current density measured at two different overpotential values of 400 mV and 500 mV for all the materials studied in this work. Among the composite materials investigated, NiCo-200 displays a better electrocatalytic activity for OER at these two overpotential values.

Among the remaining composites namely NiCo-400, NiCo-600 and Ni-600 (M = Ni or Co), NiCo-600 showed a higher catalytic activity towards OER in KOH solution than NiCo-400 and Ni-600. Also the activity of NiCo-400 is higher than that of Ni-600. Significantly, at $j = 10$ mA/cm², the overpotential values required for water electrolysis are determined to be 510 mV, 480 mV and 600 mV for NiCo-400, NiCo-600 and Ni-600 respectively. At $j = 20$ mA/

Table 2 Various electrocatalytic parameters such as overpotential values measured at two different current density values, Tafel slope, TOF and charge measured under the oxidation peak determined for the different binary NiCo composites and for the control samples

Sample	η_{10}	η_{20}	Tafel slope	TOF	Charge under the peak (q^*)
Ni-200	440	530	189	0.0193	0.85×10^6
NiCo-200	420	480	157	0.0234	1.22×10^6
NiCo-400	510	610	174	0.0038	0.61×10^6
NiCo-600	480	550	118	0.0041	0.40×10^6
Ni-600	600	760	118	0.0016	0.16×10^6

η_{10} , η_{20} —overpotential values in mV measured at 10 mA/cm² and 20 mA/cm² current density respectively, Tafel slope in mV dec⁻¹, TOF at 420 mV (overpotential) in s⁻¹ and charge in mC/cm² mg

cm² these values are found to be 610 mV, 550 mV and 760 mV respectively. Here it is noted that even though NiCo-400 forms pre-OER MOOH intermediate peak with higher charge density than NiCo-600, the OER activity is lesser than NiCo-600. This reversal behaviour is due to the weak crystallinity of NiCo-400 as evident by the broad peaks observed in XRD spectrum. Since NiCo-600 is having higher crystallinity as evidenced from XRD, conductivity of the base layer is more for NiCo-600 than NiCo-400. Moreover, NiCo-400 is predominantly composed of micropores that are blocked by the micro-bubbles produced during oxygen evolution [50]. The crystallinity of Ni-600 is even higher than NiCo-600 yet the charge density under MOOH peak is lower indicating that there is less accessibility of active sites which can be related to its low BET surface area value (Table 1). Moreover electrochemical active surface area (ECSA) values of these materials are also calculated by measuring the double layer capacitance values in the non-faradaic region from CV studies. The double layer charging current values are proportional to the scan rate and the corresponding double layer capacitance values are extracted by plotting the capacitive current as a function of scan rate. From these plots the corresponding double layer capacitance values are measured and subsequently these values translate into ECSA values of 6.20 cm², 4.56 cm² and 5.80 cm² for NiCo-200, NiCo-400 and NiCo-600 respectively. These values also correlate with the observed electrocatalytic behaviour for OER suggesting the enhanced accessibility of the electrolyte and hence the increased catalytic characteristics for OER. Finally the order of increasing catalytic behaviour is given as, NiCo-200 > NiCo-600 > NiCo-400. These results corroborates very well with the observation from LSV studies shown in Fig. 6A.

Different characteristic parameters associated with OER like electrochemical active surface area, Tafel slope and

turn over frequency (TOF) are calculated to obtain insights about electrocatalytic behaviour of these NiCo composites. Tafel slopes are meant to describe the OER kinetics that are analysed by plotting log i versus overpotential in the steady state region as shown in Fig. 6C. The Tafel slope values for IrO₂, NiCo-200, NiCo-400, NiCo-600, Ni-200 and Ni-600 are determined to be 139, 157, 174, 118, 189, and 118 mV/dec respectively. Tafel slope is essentially derived to obtain mechanistic information under steady state condition where the surface coverage, θ is assumed to be either 0 or 1. But in practice, the overall electrocatalytic activity of the material is associated with the variation of the surface coverage of adsorbed species with respect to potential [51, 52]. Therefore the calculated Tafel slopes in this work are found to be non-linear with the overpotential requirement at 10 mA/cm² current density.

In order to support and verify the OER activity, the voltammetric charge (q^*) of the anodic peak corresponding to the formation of metal oxyhydroxide, $M^{2+} + OH^- \rightarrow MO(OH)$ is obtained by integrating the Faradaic region under the peak as shown in Eq. (8). Further TOF values are calculated by substituting the value of scan rate (v in V/s), amount of loading (m in mg), and electrode area (A in cm²) in the Eq. (9) shown below [53].

$$q^* = \frac{1}{vms} \int_{E_1}^{E_2} i(E) dE \quad (8)$$

where E_1 and E_2 are the onset and terminal potential values of the metal oxyhydroxide peak during the anodic sweep. The results are summarized in Table 2. A higher value of 1.22×10^6 mC/cm² mg is obtained for NiCo-200 suggesting its better electrocatalytic activity than the other NiCo based composites. Further, TOF values of these catalysts are calculated for the assessment of OER activity. These values are estimated to determine the rate of oxygen evolution per second using the Eq. (9) [54].

$$TOF = \frac{j \times A}{4Fm} \quad (9)$$

where j is the current density in mA/cm², A is the area in cm², F is the Faraday's constant which corresponds to 96484.5 Coulombs and m is the number of moles of the active material or catalyst used. The corresponding TOF values are shown in Table 2. The highest TOF value of 0.0234 s⁻¹ is calculated for NiCo-200 and this value is very much closer to the previously reported nickel based catalyst for OER [53].

Finally durability of these catalytic materials is analyzed by carrying out the stability studies over a period of about 48 h by keeping the constant applied potential of 1.71 V versus RHE for NiCo-200 and at 1.78 V versus RHE for NiCo-600 using chronoamperometry (CA) studies as

well as using CV at a faster scan rate of 30 mV/s for 300 cycles between the potential window of 1.068 V to 2.068 V versus RHE in 1 M KOH aqueous solution [ESI; Fig. S9]. Figure 6D shows CA curves obtained for stability studies of the catalyst namely NiCo-200 (a) and NiCo-600 (b). The current density increases steadily during the initial period and thereafter maintained a steady state current indicating the good stability of NiCo-200. The initial increment of current density is due to kinetically controlled reactions at the interface and the later region is controlled by diffusion process [55]. NiCo-600 also shows a similar trend in CA which also exhibits an initial incremental step and later on attains a steady state. The stability assessment at a fixed scan rate of 30 mV/s reveals that both NiCo-200 and NiCo-600 after 300 cycles retain almost the same overpotential at 20 mA/cm² current density. An increase in overpotential of 30 mV is observed for NiCo-200 while there is depletion in overpotential of 30 mV is observed for NiCo-600. The activity change with respect to time is negligible which implies the higher stability of NiCo-200 and NiCo-600 on the electrode surface.

From Table 2, it is observed that higher electrocatalytic activity of NiCo-200 is due to increased number of active sites (from TOF) and enhanced electrochemical active surface area as revealed by its intermediate formation (from q*). Tafel slope in turn provides the mechanistic insight into the overall electrocatalytic process. Moreover, the obtained results are compared with the previously reported Ni and Co based composites [ESI; Table S8] and are in acceptable range of overpotential suggesting the potential use of these materials as sustainable electrocatalysts for OER in alkaline medium.

4 Conclusions

In summary, highly porous, binary NiCo metal oxide/hydroxide sponges with tunable nanostructure, morphology and porosity are prepared using a novel bio-source namely, cyanocobalamin (CB) by annealing at different temperatures. Structural, morphological, compositional and crystalline characteristics are analyzed by multiple characterization techniques including spectroscopic and microscopic studies. As-prepared materials possess different types of porosity and cellular arrangement. Further these binary NiCo metallic sponges are explored for OER studies in alkaline medium. The electrocatalytic activity is found to be better for metal hydroxides than metal oxides. Among the many different composites, NiCo-200 is found to be higher performing electrocatalyst due to the presence of residual carbon, higher crystalline nature and hydrophilic interface arising from the presence of polar groups. Moreover, NiCo-600 is found to be more active

than NiCo-400 inspite of its low surface area. This is attributed to lower crystallinity and the presence of micropores in case of NiCo-400. Finally NiCo-200 and NiCo-600 have shown good stability and retained the current density of 20 mA/cm² for a longer duration. These results clearly demonstrate the potential utility of such porous, binary NiCo metallic sponges as OER electrocatalyst for sustainable alkaline water electrolysis.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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