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Graphene Nanoclusters Embedded Nickel Cobaltite Nanofibers as Multifunctional Electrocatalyst for Glucose Sensing and Water- splitting Applications

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ABSTRACT

Nickel cobaltite (NCO) attains the apex of Sabatier-type volcano plot for electrochemical reaction compared to simple oxides due to synergetic effect of mixed transition metal cations. The combination of high surface area, aspect ratio, and porosity of electrospun NCO nanofibers (NCO-NF) enhance their electrocatalytic performance by improved electron mobility and more active sites. In the present study, NCO-NF fabricated using poly(styrene-*co*-acrylonitrile) (SAN) as a sacrificial polymer, were embellished with graphene nanoclusters (GNC), which augment the electrocatalytic performance of the NCO-NF. The in situ formed GNC along the NCO-NF are result of the interaction between the polar functional groups of the polymer, and the cations of precursor salts during the calcination of precursor nanofibers. The GNC/NCO-NF with least crystallite size and high aspect ratio having porous NCO nanoparticles and in situ grown GNC were developed using sol-gel electrospinning process assisted by calcination of precursor nanofibers. This simple, eco-friendly, and economical synthesis route with unique structure chemistry of SAN to form GNC and the presence of dual cations (Ni and Co) provides enhanced performance and multifunctionality to GNC/NCO-NF electrodes for electrocatalytic applications, such as biosensors and water-splitting. In the present study, the modified electrodes (GNC/NCO-NF/graphite electrode) exhibited excellent non-enzymatic glucose detection over a wide range of concentration with a lower limit of 1.2 μM and sensitivity of $1827.5 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{mg}^{-1}$ in 0.1 M NaOH. Further, the modified electrodes were also tuned for H_2O_2 detection to aid enzymatic glucose sensing. When examined for bifunctional water-splitting in 1 M NaOH, the electrode reached an onset potential of -0.537 V and 0.735 V against reversible hydrogen reference electrode and a Tafel slope of $37.6 \text{ mV} \cdot \text{dec}^{-1}$ and $67.0 \text{ mV} \cdot \text{dec}^{-1}$ for hydrogen and oxygen evolution reactions, respectively. The results prove that GNC/NCO-NF are promising candidates as multifunctional electrocatalyst.

Keywords: Electrospinning; NiCo_2O_4 ; graphene; sensor; electrocatalyst.

Highlights

1. Graphene nanocluster/NiCo₂O₄ (GNC/NCO) nanofibers exhibits multifunctional electrocatalytic behaviour.
2. Lower limit of glucose detection and sensitivity: 1.2 μM and $1827.5 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{mg}^{-1}$.
3. Response time for glucose and H_2O_2 sensing is 6 and 1.6 s, respectively.
4. Tafel slopes for hydrogen and oxygen evolution reaction: 37.6 and 67.0 $\text{mV} \cdot \text{dec}^{-1}$.

Graphical abstract

1. Introduction

Transition metal oxide nanofibers are promising candidate materials for electrocatalysis given the earth crustal abundance of these metals as well as the size benefits associated with nanofibers. The high aspect ratio and high specific surface area of nanofibers enables efficient charge transportation, which especially makes them attractive for electrocatalytic applications such as biosensors [1] and energy harvesting devices [2,3]. For example, simple transition metal oxide nanofibers like Co_3O_4 , CuO , NiO , TiO_2 have shown immense potential for non-enzymatic glucose sensing [1], which boosts the health industry through improved management of diabetes [4–6]. Another emerging area of their application is in electrocatalytic water splitting for hydrogen production [7], due to the increasing need for renewable energy technologies. A variety of techniques have also evolved over the last decade, which facilitate the easy synthesis and fabrication of transition metal oxide nanofibers [8,9]. All these factors motivate studies for developing transition metal oxide nanofibers with enhanced catalytic and sensing properties as well as to improve our understanding of the underlying mechanisms.

Among transition metal oxides, nickel cobaltite (NiCo_2O_4) has seized the field of supercapacitors [10], biosensors [11] and electrocatalysis [12]; due to its remarkable oxidation states and better electrical conductivity than simpler oxides like NiO or CoO_x [13]. Extensive studies on glucose detection and water oxidation have been reported in literature using NiCo_2O_4 (NCO) in the form of various nanostructures [11,14,15], hybrid composites [16–18] and carbon-based composite materials [19,20]. Previously, electrospun NiO and Co_3O_4 nanofibers have been explored for use in biosensors for glucose monitoring [21,22] and as cells for electrocatalysis [23]. It was soon realized that NCO exhibits superior performance due to its high electronic conductivity and presence of plenty of active sites. NCO has spinel structure, where octahedral cations are easily accessed by electrolyte at the interface [11,24]. Apart from these, graphene-based materials have been explored in depth for various electroanalytical methods [25]. Hence, NCO has been extensively investigated in the presence of graphene derived materials, and their combination showed an excellent electrocatalytic performance towards glucose sensing and oxygen reduction reaction than NCO alone due to the synergistic effect of heterostructures [19,20,26,27]. Another important aspect of glucose sensing is that the oxidation of glucose is always associated with the production of H_2O_2 . Hence the first-generation glucose sensors were based on H_2O_2

detection. Given this, it is important that studies involving electrocatalytic and glucose sensing properties of NCO be also conducted in presence of added H_2O_2 . Furthermore, the enzymatic glucose detection is always associated with the H_2O_2 liberation and sensing [28]. In addition, electrocatalytic H_2O_2 detection has been major focus in biological, pharmaceutical, food, and textile manufacturing applications [5]. Therefore, H_2O_2 detection is an essential aspect of biosensing applications, along with glucose sensing, and in the process, it is also important to avoid interference from other organic and inorganic moieties present with glucose. Some of these species are ascorbic acid, lactic acid, uric acid, dopamine, tryptophane, glycolic acid, L-valine, L-proline, L-lysine, sucrose, fructose, maltose, carragene, NaCl, and cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Zn^{2+}) [11,13,14,17,28–33].

The focus of the present work was to study the electrocatalytic behaviour of NCO nanofibers (NCO-NF) synthesized by sol-gel assisted electrospinning in which styrene acrylonitrile copolymer (SAN) was used as a binder and viscosity modifier. This process led to the formation of NCO-NF decorated with *in-situ* graphene nanocluster (GNC), which is novel using SAN as a result of cyclisation and graphitisation of randomly situated functional groups (styrene and nitrile) of SAN in the presence of Ni and Co compounds. The presence of functional groups in SAN and the interaction of Ni/Co cations with these functional groups helps in formation of GNC material along the NCO-NF (Figure S1). This *in-situ* grown GNC are more entrenched and bridged with NCO particles as they grow along with the NCO particles. Therefore, they are attributed with better inter-particle interactions as well as particle-electrolyte interaction than when graphene derivatives are added separately to NCO nanoparticles for electrocatalytic reactions [34]. Apart from this, the NCO nanoparticles are decorated along the mesoporous nanofibers that enhances their charge transportation efficiency, as well as increases the surface area available for electrocatalytic reactions. This unique *in-situ* technique for GNCs using SAN as a polymeric binder in sol-gel electrospinning assisted by calcination of precursor nanofibers, provides a simple, eco-friendly, and economical synthesis route to develop an NCO-NF or NCO-NF composites (with or without organic or inorganic materials as fillers) with better morphological, physico-chemical, and electrocatalytic properties. And, the GNC/NCO which was developed with this synthesis technique has an enhanced or comparable performance than other Ni or Co or NCO based electrocatalyst in literature. Given these unique advantages, the electrocatalytic performance of this GNC/NCO was characterized by using it as an electrocatalyst in three different reactions: glucose detection, H_2O_2 detection, and water electrolysis.

2. Materials and methods

D-glucose and sodium hydroxide (NaOH, pellets) were procured from Nice Chemicals, Mumbai, India. Hydrogen peroxide (H_2O_2 , 30% w/v) was bought from Spectrum Reagents and Chemicals Private Limited, Mumbai, India. The poly(vinylidene fluoride) (PVDF, Solef® 1015, Solvay, Italy) polymer of wt average molecular weight of 575,000 was purchased from Prakash Chemicals Private Limited, Gujarat, India. N, N-dimethylformamide (DMF) was obtained from Sisco Research Laboratories Private Limited, Taloja, Maharashtra, India. All chemicals were of assay > 99% and were used without further purification.

GNC/NCO-NF were synthesised by sol-gel assisted electrospinning process, followed by calcination of electrospun precursor nanofibers at three different calcination soaking times, t (i.e. 2, 4, and 6 h) and temperature of 500°C (optimal for NCO growth). Hereafter, the GNC/NCO-NF synthesised using calcination soaking time of 2, 4, and 6 h will be mentioned as NCO-2, NCO-4, and NCO-6, respectively. The detailed synthesis and characterization techniques of GNC/NCO-NF were explained in our earlier work [34]. The nanostructure morphology and selected area diffraction pattern of polycrystalline GNC/NCO samples were studied using high-resolution transmission microscope (HRTEM, JEM 2100, JEOL, USA). X-ray diffraction (XRD) patterns were recorded to study the phase purity and crystallinity of GNC/NCO-NF, using x-ray diffractometer (DXGE-2P, JEOL, Japan) with monochromatic Cu K_α radiation ($\lambda = 0.154$ nm).

The non-crystalline phase, electronic and structural features of GNC/NCO-NF such as band gap energies, defects, and elemental composition were analysed using diffuse reflectance UV-vis-NIR spectrometer (3600+, Hitachi, Japan), photoluminescence (PL) emission spectrometer (Fluoromax-4 Spectrofluorometer, Horiba, France) and x-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Scientific, USA). The absorption spectra of samples were acquired in the wavenumber range of 5 – 50 cm^{-1} , and the emission spectra were obtained in the wavenumber range of 17 – 28 cm^{-1} utilizing an excitation source of 325 nm wavelength. Determination of oxidation states of the constituent elements and the depth profiling of GNC/NCO-NF were done using XPS, deploying a monochromatic Al K_α radiation (1486.6 eV). The Ar^+ ion beam etching was performed for 25 s to attain a new surface at each depth.

All electrocatalytic studies were carried out using an electrochemical workstation (SP-150, Bio-Logic Science Instruments, France) with three electrode configuration and test set-up as shown in **Figure 1** at an ambient environment. The electrolyte and analyte solutions were prepared with Millipore water ($18.2 \text{ M}\Omega\cdot\text{cm}$ resistivity), which was purged with nitrogen gas for 20 min to remove the dissolved oxygen in the solution prior to experiment. The modified cylindrical graphite electrode (GE) with 1 cm diameter served as the working electrode, whereas saturated calomel electrode (SCE) was used as a reference and platinized platinum as a counter electrode. The GE ends was polished to glassy surface and the walls were insulated with Teflon tape. The polished ends were cleaned by ultrasonication with Millipore water for 30 minutes and air dried. One end of the polished surface was used for electrical connections using soldering and insulation, and the other end was loaded with the catalyst ink.

The catalyst ink was prepared by sonicating 10 mg GNC/NCO-NF in 1 mL of ethanol. For sensing studies, 40 μL of this suspension was loaded on the polished surface of GE and air dried for 10 min, while 1 mL of the catalyst ink was dropped on the polished surface of GE for hydrogen evolution reaction (HER) or oxygen evolution reaction (OER) studies. After the deposit dried, 10 μL of 0.5% solution of PVDF in DMF was dropped on the deposit to keep the GNC/NCO-NF deposit intact on the electrode. The same amount of PVDF/DMF solution alone was loaded on the polished surface of GE to account as bare electrode. The electrode was dried in air for 6 h to ensure that any residual solvents were removed. The electrodes were submerged in 0.1 M NaOH electrolyte for electrocatalytic sensing application and open-circuit potential was applied for one hour to attain equilibrium before each sensing study. NaOH (1 M) was used as an electrolyte and similar steady state open-circuit potential test was acquired for water-splitting experiments. The electrolyte was continuously stirred at 100 rpm during all electrocatalytic measurements to ensure homogeneity of analyte in electrolyte during sensing, and to avoid the bubbles/gas accumulation on the electrode surface in HER or OER studies. Cyclic voltammetry (CV), Linear sweep voltammetry (LSV), Chronoamperometry (CA), Electrochemical impedance spectroscopy (EIS), and Chronopotentiometry (CP) responses were acquired to study the electrocatalytic behaviour of GNC/NCO-NF.

3. Results and discussion

3.1. Morphology and crystallinity

Figure 2a-c shows an HRTEM image of NCO nanoparticles deposited on GNC. The evolution of NCO and GNCs during calcination of precursor nanofibers is explained in detail elsewhere [34]. In addition to HRTEM images, the confirmation of GNCs were further confirmed using XPS, UV-vis-NIR, PL in our previous study [34]. The GNC structure seems to decrease and diminish with increase in calcination soaking time due to thermal degradation. A thick layered structure was observed for NCO-2, which transforms to almost single layer for NCO-4 and slowly, diminishes for NCO-6. This suggests that the NCO-4 consists of less agglomerated and well-bridged GNC in between the NCO nanoparticles that in turn, improves the electrical/ionic conductivity of the NCO-4 nanofibers. Furthermore, the increased porous structure in NCO nanofibers would predominantly reinforce the surface efficiency and improve the diffusion kinetics of electrolytes into the NCO samples, during electrocatalytic reactions. It can be seen from Figure 2a-c, that the porosity of NCO-4 is moderately higher than that of NCO-2 and NCO-6, where the particles are loosely packed with interparticle voids (Figure 2a-f). This is attributed to the crystallite splitting phenomenon as confirmed by XRD crystallite analysis and porosity analysis (from Ref. [34]), which provides a larger surface area for the catalyst to improve its catalytic performance.

A well-resolved lattice fringes of corresponding diffraction crystal planes, with respective d -spacing of NCO, for all three samples are shown in Figure 2d-f. The SAED patterns of the polycrystalline GNC/NCO samples are seen in Figure 2g-i, which were indexed to the XRD planes of diffraction which correspond to NCO. The inset Figure 2g-i, shows XRD patterns obtained for the samples at different t , and the diffraction peaks were indexed to the reflection planes of the reference spinel NCO of *The International Centre for Diffraction Data* (ICDD) file no. 01-073-1702. No XRD peaks or SAED patterns were observed for GNC and this implies that the structure is non-crystalline, which is in good agreement with the Raman spectroscopy from our previous study [34]. The average crystallite sizes of NCO crystallites calculated for all the three GNC/NCO samples were in the range of 14 – 17 nm, and a lower one was for NCO-4 due to crystallite splitting phenomena (thermodynamically driven mechanism or mechanical rupture of crystallite splitting within the particle in the presence of crystal splitting or defects or foreign materials such as doped elements, graphene, etc. during the crystallite growth) [34]. It must be noted

that apart from point defects, dislocations in the crystallite act as active sites for electrochemical reactions.

The dislocation density (ρ_D) is defined as the length of dislocation lines per unit surface of the crystal and is given by $\rho_D = \tau/D^2$, where τ is a factor, which is equal to unity for minimum dislocation density [35]. Using the average crystallite sizes (D) of NCO-NF as obtained from XRD analysis in Ref.[34], the dislocation densities (ρ_D) in NCO crystallites were estimated to be 3.82×10^{11} , 4.82×10^{11} , and 3.58×10^{11} lines·cm⁻² for NCO-2, NCO-4, and NCO-6, respectively. Another method of estimating ρ_D in NCO crystallites on basis of XRD analysis for close-packed cubic system was implemented using Ref.[36] & [37] (Section S2, ESI) and found to be 1.74×10^{11} , 2.19×10^{11} , and 1.63×10^{11} lines·cm⁻². It has to be noted that D is a function of lattice strain, lattice parameter, and other assumed factors as explained in Section S2, ESI. From both methods, the ρ_D is the highest for NCO-4, which influences the electrochemical reactions, because the charge-transfer resistance decreases with increase in ρ_D [38]. This suggests that NCO-4 will have a better electrocatalytic activity.

3.2. Structural defects and non-crystallinity

XPS surface analysis was conducted on all the GNC/NCO samples to analyse their catalytic effect. The elemental composition of all the samples were similar as seen from the investigation of earlier work [34]. Further, in this study, a depth analysis of NCO-4 was done to avoid the atmospheric contamination and surface defects. XPS survey spectrum of NCO-4 (Figure S2, ESI) shows the peaks corresponding to Ni Co 2p, Co, O, and C for NCO-4 at surface and two depths (S, T, and U stands for surface, depth obtained after 25 s of Ar⁺ ion etching, and depth obtained after 50 s of Ar⁺ ion etching, respectively). The Ni 2p high-resolution spectrum in Figure 3a-c conforms to the doublet spin-orbit of $2p_{3/2}$ (ca. 853 eV) and $2p_{1/2}$ (ca. 871 eV) electronic configuration with corresponding shake-up satellite peaks denoted as *sat*. Each of the above peaks have been deconvoluted to the characteristic peaks of Ni²⁺ and Ni³⁺ [11,16].

Similarly, Co doublet electronic configurations were conformed at binding energies of ca. 779 eV and 794 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively. Furthermore, the deconvolution of Co 2p high-resolution spectrum showed the characteristic of peaks assigned to Co²⁺ and Co³⁺

along with its respective shake-up satellite peaks (*sat*, Figure 3d-f) [11,13]. These results are in line with the early literature and confirmed that both trivalent and divalent cations are well distributed on the surface and coactive to contribute to electrocatalytic reactions. The trivalent cations are expected to aid in the electrochemical process by fast charge transportation across the electrode-electrolyte interface [13]. Also, the ample intrinsic redox couples of cations (M^{2+}/M^{3+}) well distributed in mesoporous NCO nanoparticles could enhance the electroactive sites for catalysis reactions [11].

Figure 3g-i shows the O 1s high-resolution spectrum at S, T, and U of NCO-4 sample. The deconvoluted peaks reveal the presence of inverse spinel lattice oxygen (cation replacements from parent position due oxygen vacancies) [39] and C=O functional groups around binding energies of ca. 528 eV and ca. 530 eV, accordingly [13]. The peak at ca. 532 eV can be attributed to the sorbed oxygen moieties on the surface of NCO-4. Furthermore, in Figure 3j-l of C 1s high-resolution spectrum, the deconvoluted peak at ca. 284 eV was ascribed to C=C/C-C of graphene. The peaks between 285-290 eV belong to the oxygenated carbon species such as C=O and C-O, which are attributed to defects in GNCs (surface or edge) due to oxidation during the synthesis process [13,34,40]. All the carbon-based peaks are ascribed to GNCs and oxidized GNCs, which are in good agreement with optical spectroscopies results (Section S4, ESI) and our previous study [34]. Henceforth, achieving the *in-situ* formed GNCs due to the synergetic presence of functional groups of SAN polymer and cations. It has to be noted that even though GNC/NCO were synthesised at controlled calcination conditions (Section 2), the growth of GNCs are non-homogenous in NCO-NF as the SAN is a random co-polymer and the growth of GNCs is expected only at the blocks of nitrile functional groups in the SAN [41]. This suggests that SAN is an potential and efficient polymeric binder to develop GNC/metal-oxide nanofibers from sol-gel electrospinning process assisted by calcination.

Additional peaks arise around binding energies of 280 eV and 292 eV in Figure 3k and 3l as the sample is etched along the depth of the NCO-NF, which correspond to C-O-M i.e. metal oxide/C interface (reason for GNC formation in presence of cations) [42] and characteristic shake-up satellite of graphene [40], respectively. This suggests that the GNCs are grown as template/substrate structures in between the NCO nanoparticles, which enhance the electrocatalytic performance of NCO-NF. Further, the supplementary peaks in Figure 3l around 295 eV and 297 eV are due to oxidation of carbon-based material (CO_2 formed are

adsorbed on cations) [43] and surface charging [44], respectively, as a result of Ar⁺ ion etching during XPS analysis. The presence of GNC boosts up the electrocatalytic activity due to the presence of large surface area, active (defective) sites (by physic or chemisorption), and enhanced electrical/ionic conductivity [13,26,32]. Hence, the GNC/NCO composite nanofibers were expected to be suitable for the electrocatalytic process with significantly improved sensitivity in detection of analytes.

3.3. Electrocatalytic sensing behaviour of NCO-NF

Figure 4a shows typical CV curves acquired for the bare GE and GNC/NCO/GE under the applied potential from 0 to 0.7 V in 0.1 M NaOH electrolyte in presence of 1 mM glucose. For NCO-4 with 1 mM glucose, two pairs of anodic peaks at ca. 0.32 V (labelled A) and 0.48 V (labelled B), as well as cathodic peaks at ca. 0.20 V (labelled C) and 0.40 V (labelled D) were observed which can be ascribed to the reversible redox reactions of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺ [14,21]. On the contrary, no redox peaks were found for bare GE in the presence or absence of glucose (Figure 4) as no such redox reactions occur. The redox reactions of NCO in basic alkaline electrolyte are [29]:

Among the three NCO/GE samples, the area enclosed by the CV curves is the largest for NCO-4/GE, which suggests that NCO-4 has higher electrocatalytic activity than the other samples. This may be explained through a combination of several factors such as the greater surface area arising from the more porous structure, enhanced active sites obtained by crystalline splitting [14,34], multiple band gaps, and the less agglomerated GNC [26]. Besides, it has been reported in literature that the electrocatalytic activity of NCO increases in the presence of NiO. This is partly due to the increased surface cation concentration. Additionally, Ni²⁺ → Ni³⁺ oxidation occurs at more negative potential than Co³⁺ → Co⁴⁺ [24], which is responsible for sensing behaviour. A closely related phenomena is the transformation of inverse spinel to normal spinel with increase in calcination soaking time [45]. Essentially, the Ni cations meet the electrolyte at the surface of the material as they move from tetrahedral to octahedral voids in the crystal structure and facilitates fast electron transfer across the interface [13,29]. However, maintaining an optimal soaking time is also

necessary as the particle shape needs to be retained. Along similar reasoning, one may expect that NCO-4 would manifest better electrocatalytic performance.

The CVs corresponding to NCO-4/GE at different concentrations of glucose are shown in **Figure 4b** in the applied potential range of 0-0.8 V. It is clear that the NCO-4/GE exhibits a significant increase in the anodic peak current after the addition of glucose, which suggests better electrocatalytic activity of NCO-4 nanofibers towards glucose oxidation. The electrocatalytic mechanism of the GNC/NCO exposed to glucose in alkaline electrolyte can be described by the following equations [14,33]:

First, the Ni^{2+} and Co^{2+} cations from NCO oxidise to Ni^{3+} and Co^{3+} species due to the applied voltage by losing two electrons. This is the reason for the higher anodic peak current of NCO/GE compared to bare GE. Then, upon addition of glucose to the electrolyte, glucose oxidises to gluconolactone by transferring two electrons to the electrolyte and thus a further increase in the anodic peak current is observed. The oxidation of cations and glucose occur simultaneously at the same applied voltage, but the rate of oxidation of cations at the surface of the NCO-NF determines the rate of detection of glucose. Nevertheless, it can be concluded that glucose sensing is an intrinsic electrocatalytic property of NCO-NF and it can be tuned by controlling the morphological structure and electronic properties of the material.

The electrocatalytic sensing properties of bare GE and NCO-4/GE were evaluated at various H_2O_2 concentrations. **Figure 4c** shows the relevant CV curves. The positive anodic current for NCO-4 without H_2O_2 comes from the oxidation of cations, as described in **Equation (3)**. The increase in oxidation current by upon addition of H_2O_2 in NaOH can be attributed to the oxidation of H_2O_2 as:

In the CV curves of NCO-4/GE with 100 μM and 400 μM H_2O_2 , the anodic peaks at ca. 0.35 V and ca. 0.5 V and the cathodic peaks ca. 0.2 V and ca. 0.4 V represent the redox couples of **Equations (1) and (2)**, respectively. The higher anodic peak current with increasing H_2O_2 concentration indicates good electrocatalytic activity of GNC/NCO-NF for H_2O_2 oxidation. A

plausible reaction mechanism for NCO with H_2O_2 in alkaline medium has been proposed in literature [46,47]:

where M represents both Ni and Co cations. Essentially, the divalent cations (M^{2+}) transfer electrons from oxygen atoms of H_2O_2 to form a complex species as shown in **Equations (6) and (7)**, which eventually results in the formation of trivalent cations (M^{3+}). Subsequently, the $O-O$ bond elongation and electron distribution takes place, and OH^- ions are released to the electrolyte along with oxidation of cations in GNC/NCO-NF.

Figure 5a shows the CV curves of NCO-4/GE at various scan rates (20 to 250 $mV \cdot s^{-1}$) in the presence of 1 mM glucose in NaOH electrolyte. The anodic and cathodic peak currents increase with increasing scan rate. Both the anodic and cathodic peak currents appear to satisfy a linear fit with the scan rates, as seen from **Figure 5b**. This demonstrates that electrocatalytic process for glucose detection is kinetically controlled as previously suggested [13].

3.4. Amperometric detection

The CA analysis was carried out to estimate the detection limit and sensitivity values of NCO-4/GE in 0.1 M NaOH electrolyte (pH 13 and scan rate = 100 $mV \cdot s^{-1}$). An optimal steady-state potential for analyte electrocatalytic performance was obtained by performing LSV at a slow scan rate (i.e. 2 $mV \cdot s^{-1}$). These optimal steady-state potentials vs. SCE were found to be 0.53 V and 0.6 V for glucose and H_2O_2 detection, respectively (**Figure S5, ESI**).

Figure 6a shows a typical CA response of NCO-4/GE upon successive addition of glucose into constantly stirred electrolyte. The successive addition of glucose concentration was in the range of 50-1100 μM . The sensor responded swiftly upon addition of glucose at each step and the steady state current was reached in ca. 6 s (**Figure 6c**). Also, the sensor showed a step-like increase in response current with successive addition, which may be attributed to the homogenous electrocatalytic activity and enhanced conductivity obtained in

NCO-4 nanofibers. **Figure 6b** displays the calibration curve for glucose detection, obtained by measuring the current change with each incremental addition of glucose, and plotting the same against the specific concentration of glucose. As seen in **Figure 6b**, the response of the sensor shows a linear relationship towards glucose for the concentration of 50-400 μM and 400-1100 μM with a correlation coefficient of ca 0.989 and sensitivity values equal to 1827.5 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{mg}^{-1}$ and 1072.5 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{mg}^{-1}$, respectively. The limit of detection (LOD) and limit of quantification (LOQ) of the CA glucose sensor were estimated using **Equations (5) and (6)** [29]:

$$LOD = (3S_b) / m \quad (5)$$

$$LOQ = (10S_b) / m, \quad (6)$$

where S_b is the standard deviation of blank signal for ten measurements (0.000302 mA) and m is the slope value extracted from the calibration plot. Thus, the calculated LOD and LOQ for glucose sensor in the linear region of 50-400 μM were 1.2 μM and 4.1 μM , respectively.

The typical CA response for NCO-4/GE for an optimal applied voltage of 0.6 V, with successive addition of H_2O_2 (20-700 μM) is shown in **Figure 7a**. The sensor response towards H_2O_2 was more rapid as compared with that towards glucose, which achieved a steady-state current within ca. 1.6 s (**Figure 7c**). This rapid increase in response time indicates exceptional electrocatalytic oxygen evolution reaction performance of NCO/graphene material [48]. By measuring the change in current for the corresponding addition of H_2O_2 , a calibration plot was designed akin to that of glucose. Here in **Figure 7b**, again two regions of linear fits were found for different range of H_2O_2 concentration, i.e., 20-200 μM for lower concentration ($R^2 = 0.959$) and 200-700 μM for higher concentration of H_2O_2 ($R^2 = 0.932$). The sensitivity of H_2O_2 , for these two regions of response were 1322.5 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{mg}^{-1}$ and 427.3 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{mg}^{-1}$, subsequently. The LOD and LOQ for H_2O_2 sensor was estimated to be 1.7 μM and 5.7 μM , respectively, at the region of lower concentration.

The selectivity of a sensor is a material property, and the literature suggests no significant interference of accompanying species with glucose or H_2O_2 detection, when NCO and NCO/graphene derived electrodes are used. Furthermore, it has been reported that NCO and NCO/graphene derived electrodes provide excellent selectivity towards analytes in the presence of interferents [11,13,14,17,28–33]. The stable and concurrent stepwise response

recorded during the successive injection of different concentrations of analytes marks the steady electrocatalytic activity. In addition, the absence of hindrance in successive stepwise response of the sensing process suggests the distinguished operational stability and repeatability of the GNC/NCO/GE electrodes.

3.5. EIS analysis

The electrical/ionic conductivity and charge-transfer properties of NCO-4/GE electrodes are influential factors of sensor activity. EIS was conducted to evaluate the physicochemical process at the surface of the electrode. The important measurements done in this context relate to the response time variation, charge-transfer capability at high frequency and mass transfer competence at low frequency. The EIS data were analysed using Nyquist plot, which represents the frequency response of electrode/electrolyte interface by examining the imaginary component ($-Z''$) of the impedance and the real component (Z'). The Nyquist plots of the sensors in the absence and presence of analytes are shown in [Figure 8a and 8b](#). It was observed that the Nyquist plot in absence of analyte ([Figure S6, ESI](#)) had a less prominent semi-circular region, and a more prominent semicircle with reduced diameter in the presence of glucose. This semicircle diameter describes the charge-transfer resistance (R_{ct}) at electrode/electrolyte interface and the substantially reduced diameter therefore suggests enhanced charge conductivity at the electrode/electrolyte interface.

Along similar lines, the diameter of the semicircle was found to be smaller in presence of H_2O_2 , which again suggests more intensified charge-transfer at the electrode/electrolyte interface. To have an insight into the interface dynamics, a simple Randles equivalent circuit ([Figure 8c](#)) was fitted to the Nyquist plots based on Bode phase plots ([Figure S7, ESI](#)) assuming defects to be present in the material. The fitted circuit is compatible with the plots, and the parameters obtained are tabulated in [Table 1](#). The low frequency regions of the Nyquist plots are not linear for both the analytes. This confirms that there was no significant mass diffusion process involved at the electrode/electrolyte interface. Hence, R_{ct} (a function of the working electrode potential and the analyte concentration) alone influence the charge-transfer rate (sensing behaviour) at the electrode during the oxidation of analytes without any diffusion impedance contribution [33]. The R_{elect} corresponds to the electrolyte resistance, Q_{CPE} and C_{dl} represent the constant phase element

and pseudo capacitance of double-layer. In case of non-ideal capacitance, i.e. material having defects, Q_{CPE} cannot be considered as capacitance and hence, C_{dl} is given by [49]:

$$C_{dl} = R_{ct}^{(1-a)/a} \times Q_{CPE}^{1/a} \quad (7)$$

where a is the exponential factor, which is equal to zero when Q_{CPE} represents pure resistor and unity when Q_{CPE} is pseudo capacitance.

From **Table 1**, it is observed that R_{ct} and C_{dl} decrease upon the addition of analytes to the electrolyte, which is synchronous with the increase in response current as seen from CV and CA [33]. The decrease in C_{dl} may be attributed to decrease in defects/active sites during the electrocatalytic reaction. Therefore, C_{dl} is the least for bare GE as no active sites/ionic species present in the vicinity of the electrode. This phenomenon also explains the diffusion of analytes from electrolyte to electrocatalytic active sites. Since R_{ct} is inversely proportional to charge-transfer rate at the electrode, the CV and CA analysis shows a decrease in R_{ct} with increase in analyte concentration. This suggests that at a higher concentration of analytes, a better sensing efficiency is possible, and at a step out, it must be noted that the normal glucose level in human blood and urine is in the range of 3.9-10 mM and 0-0.8 mM, respectively. Hence, the NCO-4/GE sensor would efficiently perform well in these regions.

Table 2 shows the comparison of glucose or H_2O_2 sensing performance of GNC/NCO nanofibers developed in the present work with some previous literature. In general, it can be seen that NCO-4/GE has comparable or better performance parameters than that of other electrocatalyst, filler, electrode, or NCO developed by different synthesis routes, in assessment with response time, linear range, limit of detection or sensitivity. Further, in comparison with those electrocatalyst having far better performance in mentioned parameters, the GNC/NCO nanofibers holds good in terms of simple, less impurities, eco-friendly, and economical synthesis route (compared to multi-stage, template-assisted, solvo/hydrothermal methods, electrodeposition etc.), *in-situ* GNCs formation that is efficient (compared to dispersion or coating method), and type of electrode substrate used that is feasible (compared to foam, conductive oxide plates or expensive metal foils).

3.6. Electrocatalytic water-splitting

The water-splitting properties of NCO-4 nanofibers are investigated through CV and CP, and Tafel polarisation studies in 1 M NaOH electrolyte medium. The steep increase in anodic current beyond 0.6 V in **Figure 4a**, corresponds to the oxygen evolution reaction through four-electron transfer process in basic medium,

CV was carried out with conventional three electrodes set-up for 50 cycles, at an optimal scanning rate of $100 \text{ mV} \cdot \text{s}^{-1}$. CV were obtained in the negative potential window of 0.0 V to -1.6 V for HER and in the positive potential range of 0 V to 0.8 V. CP study was employed to study the stability of the electrocatalytic process of HER at a constant current of -300 mA and OER at a constant current of 300 mA, for a duration of 1800 s each.

3.6.1 Hydrogen evolution reaction

The CV studies of GNC/NCO-NF were employed for HER analysis as it describes the electrode/ion interaction at the cathode. The H^+ ion from electrolyte accepts electrons at cathode and becomes a nascent hydrogen atom (chemisorbed) on the electrode surface and is later converted to H_2 gas [23]. Also, the electrocatalytic efficiency can be explained by CV using the response current, as it is a direct indicator of the adsorbed ion concentration. **Figure 9a** shows the HER CV curve for NCO-4/GE. The onset potential of H_2 was found to -0.781 V (-781 mV vs. SCE) or -0.914 V @ $10 \text{ mA} \cdot \text{cm}^{-2}$ (vs. RHE), beyond which there was a vigorous H_2 evolution and a drastic increase in the cathodic current. The present results show that the efficiency of GNC/NCO-NF as electrocatalyst is better than that of Co_3O_4 nanofibers prepared by sol-gel electrospinning in an earlier research [23].

The inset in **Figure 9a** is the CP curve obtained for HER, where at the constant applied current of -300 mA, a continuous reduction of the H^+ ions take place at the cathode surface and thereby resulting in continuous evolution of H_2 . The electrode potential attained during CP analysis at constant current depends on many factors such as, redox couples available in NCO-4, active sites, and H^+ concentration in electrolyte [50]. The CP result shows continuous evolution of H_2 for 1800 s with no significant change in the potential, which implies a promising long-term kinetic stability of GNC/NCO-NF for use in electrocatalytic water-splitting applications.

3.6.2 Oxygen evolution reaction

The OER analysis was done using CV experiments of NCO-4 nanofibers along similar lines as HER, but over a positive potential range (0-0.8 V). From the CV curve of **Figure 9b**, the onset potential of O_2 evolution was noted as 0.491 V (491 mV vs. SCE) or 0.855 V @ 10 $\text{mA}\cdot\text{cm}^{-2}$ (vs. RHE). The onset potential is the minimum potential at which the oxygen is formed at the electrode at given conditions. The obtained onset potential of O_2 evolution for GNC/NCO (0.735 V vs. reference hydrogen electrode, RHE) was found to be half the value reported for NCO/reduced graphene oxide electrode (1.57 V vs. RHE) [48] and comparable to Co_3O_4 nanofibers [23] fabricated using similar technique. This indicates the superior electrocatalytic activity of GNC/NCO/GE electrodes.

Figure 9b shows the results of electrostatic stability studies for OER using CP at a constant applied current of +300 mA. A sharp increase in potential was observed before a stable potential range is attained where OH^- is oxidised to oxygen. A stable potential is achieved, as the fresh bubbles forming at the electrode is in equilibrium with the escaping ones. The continuous evolution of oxygen for the entire 1800 s represents better kinetic stability of the electrocatalyst for OER. Furthermore, the onset potential (**Table 3**) conveys that the electrocatalytic performance of NCO-4 nanofibers is higher towards OER compared to HER due to the affinity of active sites (cations especially in octahedral sites) towards OH^- adsorption at the surface [23,51]. The Tafel polarisation plot of NCO-4 obtained by LSV at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ is shown in **Figure 9c**. The Tafel slopes for HER and OER were measured to be $37.6 \text{ mV}\cdot\text{dec}^{-1}$ and $67.0 \text{ mV}\cdot\text{dec}^{-1}$, respectively. The Tafel slope values are in agreement with the Volmer-Tafel mechanism for HER with the Tafel reaction being the rate-limiting step [12]. **Table 3** shows the comparison of water-splitting parameters of GNC/NCO nanofibers with some electrocatalyst in literature. It is observed that GNC/NCO has comparable performance in the literature. However, the electrocatalyst that out perform GNC/NCO nanofibers has a similar limitation as biosensor electrodes due to their complex, additional or expensive synthesis process and electrode substrates.

4. Summary and conclusions

The catalytic effect of precursor ions (Ni and Co) resulted in the formation of *in-situ* GNC in NCO nanofiber due to the dynamic interaction of cations with functional groups of the SAN polymer. The presence of GNC deep-seated with NCO nanoparticles along the NCO-NF

were confirmed by HRTEM and XPS depth profile analysis. The porosities, multiple band gap energies, NCO crystal defects and graphene sp^2 defects favoured significant improvement in the electrocatalytic activity of NCO towards sensing of glucose and water-splitting phenomena. Among the fibres calcined at different soaking times, NCO-4 nanofibers showed better electrocatalytic activity because of the synergistic effects of less agglomeration in the GNC, continuous links between NCO nanoparticles, and increase in defect concentration of NCO nanocrystallite by crystallite splitting

These features of NCO-4 nanofibers resulted in better sensitivity of analytes in NCO-4/GE sensors, i.e. $1827.5 \mu\text{A}\cdot\text{mM}^{-1}\cdot\text{mg}^{-1}$ for glucose and $1322.5 \mu\text{A}\cdot\text{mM}^{-1}\cdot\text{mg}^{-1}$ for H_2O_2 , over a wide linear concentration of 50-400 μM and 20-200 μM , respectively. The LOD and LOQ of both analytes were in similar range as in earlier literature. The response time for glucose detection was 6 s and that of H_2O_2 was 1.6 s, using NCO-4/GE sensor. The response time, LOD, and LOQ for both the analytes were also comparable to the earlier literature. NCO-4/GE electrodes showed good electrocatalytic water-splitting behaviour with an onset potential of approximately -0.78 V (vs. SCE) for hydrogen evolution and around 0.49 V (vs. SCE) for oxygen evolution in alkaline medium. In summary, NCO-4 nanofibers have a promising potential for multifunctional electrocatalytic activity such as simultaneous glucose detection and water oxidation in alkaline medium.

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Caption to figures

Figure 1: Schematic showing test set-up for electrocatalytic studies.

Figure 2: (a-c) HRTEM and (d-f) lattice fringe images, (g-h) SAED patterns and (inset g-h) XRD patterns of GNC/NCO-NF obtained at different calcination soaking times. Arrows in HRTEM images indicate GNC.

Figure 3: High-resolution XPS depth profiling of NCO-4 nanofibers for Ni 2p (a-c), Co 2p (d-f), O 1s (g-i), and C 1s (j-l).

Figure 4: (a) CV curves of bare GE and GE loaded with GNC/NCO-NF obtained at different calcination soaking times for a glucose concentration of 1mM. CV curves of bare GE and GE loaded with NCO-4 nanofibers in presence of (b) 1 mM glucose and (c) 100 μ M H_2O_2 .

Figure 5: (a) Cyclic voltammograms at various scan rates for GE loaded with NCO-4 nanofibers, in presence of 1mM glucose. (b) Linear fits of anodic current vs scan rates for both the cations.

Figure 6: (a) Amperometric response of NCO-4 nanofibers loaded GE for successive addition of glucose to electrolyte, (b) Response time observed for single addition of glucose, and (c) calibration curve for glucose detection using NCO-4/GE.

Figure 7: (a) Amperometric response of NCO-4 nanofibers loaded GE for successive addition of H_2O_2 to electrolyte, (b) Response time observed for single addition of H_2O_2 , and (c) calibration curve for H_2O_2 sensing using NCO-4/GE.

Figure 8: Nyquist plots for NCO-4/GE in absence and presence of analytes, (a) 1mM glucose and (b) 100 μ M H_2O_2 . (c) Randles equivalent circuit fitted for EIS spectra.

Figure 9: CV curves (inset CP plots) of NCO-4/GE obtained for (a) HER and (b) OER. (c) Tafel polarisation plot at a slow scan rate of 5 $mV \cdot s^{-1}$.

Table 1: Circuit parameters obtained for Randles equivalent fitting.

Parameter	Bare GE	NCO-4/GE in absence of analytes	NCO-4/GE in presence of 1 mM glucose	NCO-4/GE in presence of 100 $\mu\text{M } H_2O_2$
$R_{elect} (\Omega)$	23.17	28.24	28.77	31.52
$R_{ct} (\Omega)$	497300	261450	26440	277.4
$Q_{CPE} (\text{F}\cdot\text{s}^{n-1})$	0.1367×10^{-3}	1.88×10^{-3}	1.709×10^{-3}	1.904×10^{-3}
a	0.9	0.9425	0.9239	0.8779
$C_{dl} (\mu\text{F})$	218.46	2743.87	2339.17	1742.25

Table 2: Performance comparison of NCO based glucose and H_2O_2 biosensors.

Electrocatalyst and morphology (Method of filler addition)	Synthesis method	Type of electrode substrate	Analyte	Response time (s)	Linear range (μM)	Limit of detection (μM)	Sensitivity ($\mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$)	Reference
NCO-4 nanofibers (In situ GNC)	Sol-gel electrospinning assisted by calcination of precursors nanofibers	GE	Glucose	6	50-400 400-1100	1.2 2.1	930.7 576.2	Present work
			H_2O_2	1.6	20-200 200-700	1.7 5.3	673.5 216.5	
Co_3O_4 nanofibers	Sol-gel electrospinning assisted by calcination of precursors nanofibers	GE	Glucose	1.5	50-400	-	1050	[21]
			H_2O_2	6.6	20-400	-	3250	
NCO hollow nanospheres	Template-assisted	Glassy carbon electrode	Glucose	10	10-300 300-2240	0.6	1917 703	[11]
NCO hollow nanospheres/rGO	Template-assisted followed by surfactant assisted precipitation and calcination	Carbon paste electrode	Glucose	5	40-1280	0.7	2082.57	[13]
Rectangular flake-like mesoporous	Hydrothermal followed by calcination	Carbon paste electrode	Glucose	1	0.001-1900	0.0003	662.31	[14]

NCO								
NCO nanosheets	Electrodeposition	Ni foam	Glucose	-	5-90	2.46	27500	[17]
NCO-Pd nanosheets (Solution)						0.28	40030	
MoS ₂ -NCO nanoplates (Dispersion)	Hydrothermal followed by calcination	Glassy carbon electrode	Glucose	5	1-1600	0.152	1748.58	[18]
NCO/rGO (π - π interaction and dynamic potential scan)	Electrodeposition	Glassy carbon electrode	Glucose	2	10-2650	3.79	1773.61	[20]
NCO nanosheets	Electrodeposition	Indium tin oxide glass plate	Glucose	26	5-65	0.38	6690	[29]
Urchin-like NCO	Hydrothermal followed by calcination	Glassy carbon electrode	Glucose	1	0.37-2000	0.37	72.4	[31]
NCO/N-rGO/IL (Dispersion)	Hydrothermal followed by calcination	Glassy carbon electrode	Glucose	2	1-4555	0.18	3760	[32]
NCO nanorods	Hydrothermal followed by calcination	Glassy carbon electrode	Glucose	3	1-880	0.063	4710	[33]
NCO hierarchical	Sacrificial template	Stainless steel	Glucose	2	0.3-1000	0.16	1685.1	[52]

hollow nanorods	accelerated hydrolysis							
NCO	Hydrothermal followed by calcination	Three-dimensional	Glucose	-	0.5-590	0.38	2524	[53]
NiCoO ₂ nanoflakes/CNT coated with sulfonated polystyrene (Dispersion)	Template-assisted	Glassy carbon electrode	Glucose	7	10-1550	1.14	1424.41	[54]
NCO nanowrinkle/rGO (Dispersion)	Hydrothermal followed by calcination	Glassy carbon electrode	Glucose	-	5-8560	2	548.9	[55]
NCO nanoneedles (Solution and spin coating)	Hydrothermal followed by calcination	Ni foam	Glucose	10	5-15000	1.49	91.34 mV·dec ⁻¹	[56]
NCO/polyaniline (Dispersion)	Hydrothermal followed by calcination and solution mixing	Glassy carbon electrode	Glucose	5	15-4735	0.3833	4550	[57]

CNT: Carbon nanotube, N-rGO: nitrogen doped-reduced graphene oxide, and IL: ionic liquid.

Table 3: Collation of electrocatalytic HER and OER characteristics for NCO based material.

Electrocatalyst and morphology/type of electrode substrate (Method of filler addition)	Synthesis method	Onset potential of H_2 evolution (V vs. SCE)	Onset potential of O_2 evolution (V vs. SCE)	Tafel slope for HER ($mV \cdot dec^{-1}$)	Tafel slope for OER ($mV \cdot dec^{-1}$)	Electrolyte	Reference
NCO-4 nanofibers/GE (In situ GNC)	Sol-gel electrospinning assisted by calcination of precursors nanofibers	-0.781 or -0.537 vs. RHE or -0.914 vs. RHE @10 $mA \cdot cm^{-2}$	0.491 or 0.735 vs. RHE or 0.855 vs. RHE @10 $mA \cdot cm^{-2}$	37.6	67.0	1 M NaOH	Present work
Co_3O_4 nanofibers/GE	Sol-gel electrospinning assisted by calcination of precursors nanofibers	-1.26 or -1.016 vs. RHE	0.54 or 0.784 vs. RHE	-	-	1 M KOH	[23]
Hierarchical NCO hollow microcuboids/Ni foam	Sacrificial template assisted solvothermal followed by calcination	Overpotential -0.110 vs. RHE@10 $mA \cdot cm^{-2}$	1.52 vs. RHE@10 $mA \cdot cm^{-2}$	49.7	53.0	1 M NaOH	[12]
3D NCO core-shell	Hydrothermal followed	-	1.55 vs.	-	63.1	1 M NaOH	[15]

nanowires/carbon cloth	by calcination and electrochemical deposition		RHE@10 $\text{mA} \cdot \text{cm}^{-2}$				
3D hierarchical porous N-doped graphene/NCO nanosheet/porous graphene film (Solution)	Chemical and heterogenous reaction	-	1.54 vs. RHE	-		0.1 M KOH	[19]
NCO/carbon black/GE	Intermittence microwave heating	-	0.526	-	-	0.1 M KOH	[24]
NiTe/NiTe ₂ nanosheets/GE	Hydrothermal assisted anion-exchange-reaction	-	0.679 vs. RHE	-	115	1 M KOH	[50]
		-0.422 vs. RHE	-	87.4	-	0.5 M H ₂ SO ₄	
NiCo layered double hydroxide nanoplates/carbon paper	High temperature high pressure hydrothermal continuous flow reactor	-	1.597 vs. RHE@10 $\text{mA} \cdot \text{cm}^{-2}$	-	40	1 M KOH	[58]
NCO nanoneedles/FTO	Solvothermal followed by calcination	-	1.553 vs. RHE@10 $\text{mA} \cdot \text{cm}^{-2}$	-	312	1 M KOH	[59]
Au-NCO/3D hierarchical porous graphene-like/GE	Ion-exchange/activation combination followed	-	0.512	-	-	0.1 M KOH	[60]

(Au and NCO by solution and graphene-like by substrate)	by heterogeneous reaction, hydrothermal, and calcination						
3D hierarchical porous NiFe/NCO nanoflakes/Ni foam	Hydrothermal followed by calcination and electrodeposition	Overpotential -0.105 vs. RHE@10 mA·cm ⁻²	1.47 vs. RHE	88	38.8	1 M KOH	[61]
3D NCO/CuS nanowire/CFP (Solution)	Hydrothermal followed by calcination and chemical coating	Overpotential -0.0723 vs. RHE@10 mA·cm ⁻²	-	41	-	0.5 M H ₂ SO ₄	[62]
NCO/Co _{0.57} Ni _{0.43} LMOs/CFP (Solution)	Hydrothermal followed by electrodeposition and calcination	-	1.32 vs. RHE	-	63	0.1 M KOH	[63]
		-0.029 vs. RHE	-	34	-	0.5 M H ₂ SO ₄	
NCO nanowires array/FTO	Hydrothermal followed by calcination	-	1.69 vs. RHE@10 mA·cm ⁻²	-	90	1 M KOH	[64]
Au-NCO nanorod array/Ti foil (Solution)	Hydrothermal followed by calcination and deposition-reduction	-	1.59 vs. RHE@10 mA·cm ⁻²	-	63	1 M KOH	[65]

1D NCO nanowire array/Carbon rod	Hydrothermal followed by calcination	-	0.5	-	62	1 M KOH	[66]
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$E_{\text{RHE}} = E_{\text{SCE}} + 0.244 \text{ V}$, Onset potential of OER = overpotential + 1.23 V, D: dimensional, GE: graphite electrode, FTO: fluorine-doped tin oxide, CFP: carbon fiber paper, and LMO: layered mixed oxide nanosheets.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9