Multifunctional porous NiCo$_2$O$_4$ nanorods: sensitive enzymeless glucose detection and supercapacitor properties with impedance spectroscopic investigations†

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We report the multipurpose nature of NiCo$_2$O$_4$ nanorods fabricated by a facile two-step method for high-performance glucose sensors and supercapacitors. The nanorods that were obtained were investigated by various physicochemical characterization techniques, which revealed their polycrystallinity, suitable microstructure, high porosity and thermal stability. The nanorods that were synthesized were assembled on a glassy carbon electrode (GCE) with a Nafion support via layer-by-layer assembly (Nafion/NCO/GCE or NNCOGCE). The NNCOGCE that was fabricated was employed as a working electrode for two separate applications, namely, a glucose sensor and a supercapacitor. The NNCOGCE selectively detected glucose in a short amperometric response time (3 s), with a wide dynamic linear range (0.001–0.88 mM), a notable detection limit (63 nM) and high sensitivity (4.710 mA mM$^{-1}$ C$_0$$.1$ cm$^{-2}$). Moreover, the NNCOGCE exhibited high specific capacitance (980 F g$^{-1}$) at a current density of 2 A g$^{-1}$ and excellent rate performance (retention of 71.42% up to 10 A g$^{-1}$) with a long cycle life (retention of 92% up to 1000 cycles). Finally, the NNCOGCE was studied by electrochemical impedance spectroscopy (EIS) to investigate its charge transfer characteristics for both glucose sensor and supercapacitor applications, and the results were correlated with its amperometric sensing ability, as well as its supercapacitor performance.

1. Introduction

Recently, increasing demand has been observed for the design and development of smart and multipurpose materials that can be directly employed in sensors and supercapacitors.1–6 In particular, electrochemical non-enzymatic glucose sensors that depend on modified electrodes with various nanomaterials have drawn wide attention.7–20 However, the reliable detection of glucose with high sensitivity and selectivity still remains a challenge. Therefore, there is an urgent demand for reliable glucose sensors based on easily available and cost-effective nanomaterials.15–29 On the other hand, energy storage based on nanomaterials has gained tremendous interest in recent years.3,30–34 In this respect, various energy storage devices have been designed to solve the problem of the drastically growing demand for energy. Among these, pseudocapacitors have aroused immense attention because they deliver a high specific capacity.1,6,15–37 However, the energy density of pseudocapacitors is generally lower than even that of conventional batteries. Regarding this issue, mixed metal oxides have been proposed with fascinating features such as high electrical conductivity and electrochemical activity, suitable porosity and large surface areas, and also the ability to provide a wide working potential window. In this context, several bimetallic oxides such as Ru–V, Co–Ni, Mn–Ni, and Mn–Co have been reported recently as pseudocapacitor electrodes.38–44 However, the low energy density of such materials has been a persistent issue.33–46

It is to be noted that the morphology, size and porosity of electrode materials play major roles in the performance of sensors and supercapacitors.3 However, very few reports are available in which both these functions were achieved with the same electrode material.1,4 In particular, the employment of the same electrode material in glucose sensor and supercapacitor applications has rarely been reported.1

Here, we present highly porous, electrically conductive, and electrochemically active multifunctional NiCo$_2$O$_4$ nanorods fabricated by a facile method for both electrochemical glucose sensors and pseudocapacitors. So far, NiCo$_2$O$_4$ has been investigated in a specific context for either sensors or supercapacitors. To the best of our knowledge, we have studied the multifunctional...
nature of a NiCo$_2$O$_4$-based electrode for both glucose sensors and supercapacitors for the first time. In addition, the properties of the fabricated electrode have been investigated rigorously by means of voltammetric, amperometric and impedance spectroscopic methods.

2. Materials and methods

2.1. Chemicals

Nafion was procured from Sigma, and all other chemicals were procured from Merck and were used in experiments as received. Throughout the synthesis, deionized water (DI water, 18.2 MΩ cm) was used.

**Live subject statement.** Real sample experiments were performed after seeking permission from the institutional committee in compliance with the relevant laws and institutional guidelines. Ethics committee approval was obtained from the Institute Human Ethics Committee (IHEC) of IIT Indore. All procedures performed in this study were in accordance with the national laws following the Ethical Guidelines for Biomedical Research on Human Participants of the Indian Council of Medical Research (ICMR, New Delhi). In addition, verbal consent and permission were sought at the time of sample collection from the respective local diagnostic laboratory for experimentation with these samples.

2.2. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku SmartLab X-ray diffractometer using monochromated Cu Kα radiation (λ = 1.54 Å). SEM images were recorded using Supra55 Zeiss Field-Emission Scanning electron Microscope (FESEM) equipped with EDX facility. X-ray photoelectron spectroscopy (XPS) data were recorded with a PHI 5000 Versa Pro II system. TEM/SAED/ analysis was performed with a JEOL JEM-2100 system. Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo TGA/DSC 1 system using STAR$^\text{®}$ software. N$_2$ adsorption–desorption isotherms were recorded using an Autosorb iQ analyzer (version 1.11) (Quantachrome Instruments), and the corresponding pore size distribution curve was determined by the Brunauer–Emmett–Teller (BET) method.

2.3. Electrochemical measurements

Electrochemical experiments were carried out on a computer-controlled Autolab PGSTAT 204N workstation using NOVA software (version 1.10). A standard three-electrode configuration (Ag/AgCl reference electrode; platinum wire counter electrode; and a glassy carbon electrode (GCE) with a diameter of 3 mm as the working electrode) was employed for all experiments. Electrochemical measurements for the glucose sensor were performed in the voltage window of 0 to +0.6 V and those for supercapacitor testing were performed in the voltage window of −0.1 to +0.5 V at room temperature (RT) and different scan rates. Amperometry results were obtained under continuous magnetic stirring. The equations used to calculate the sensor and supercapacitor parameters are given in the ESL.$^\dagger$

2.4. Synthesis of NiCo$_2$O$_4$ nanorods

NiCo$_2$O$_4$ nanorods were synthesized by a facile two-step method comprising hydrothermal reaction followed by thermal decomposition.$^{31}$ In a typical process, cobalt acetate tetrahydrate (0.5 mmol), nickel acetate tetrahydrate (0.25 mmol), and urea (7.5 mmol) were sequentially added to and dissolved in 30 mL of a mixture of DI water (10 mL) and ethylene glycol (20 mL). The homogeneous solution that was obtained was then transferred to a Teflon-lined stainless steel autoclave (50 mL), placed in a furnace and heated for 5 h to 150 °C. After 5 h, the autoclave was cooled to RT, and a solid purple precipitate was separated by filtration and thoroughly washed with DI water and ethanol to remove any residues of ethylene glycol. Subsequently, the product was vacuum-dried at RT and then annealed at 400 °C for 3 h. Finally, a powder was collected after being cooled to RT.

2.5. Fabrication of Nafion/NCO/GCE or NNCOGCE

Initially, a glassy carbon electrode (GCE) was thoroughly cleaned, rinsed with DI water several times and dried. Subsequently, the as-synthesized powder (10 mg) was dispersed in ethanol (10 mL) by ultrasonication for 30 min. Thereafter, under optimized conditions, 5 μL of the abovementioned stable suspension (NiCo$_2$O$_4$ in ethanol) was drop-cast onto the working area of the GCE, dried in air and subsequently covered with a smooth thin layer of Nafion (5 μL, 1%). The dried modified GCE that was formed was rinsed several times with DI water and dried before being incorporated into an electrochemical workstation. The fabricated electrode was referred to as Nafion/NCO/GCE or NNCOGCE.

3. Results and discussion

NiCo$_2$O$_4$ nanorods were hydrothermally synthesized by adding M(CH$_3$COO)$_2$·4H$_2$O (M = Ni and Co) to urea in the presence of ethylene glycol, which restricts the nucleation process, and therefore the synthesis was accomplished in the absence of a template. In the first step of the synthesis, the reaction between urea and the metal salts in the presence of ethylene glycol formed a purple precipitate, and in the second step the decomposition of urea at high temperatures formed solid Ni-Co hydroxide or carbonate. Subsequently, annealing at 400 °C formed NiCo$_2$O$_4$ nanorods (Scheme 1).$^{47}$

3.1. Characterization of NiCo$_2$O$_4$

The XRD pattern of the synthesized powder reveals the cubic spinel phase of NiCo$_2$O$_4$ with lattice parameters of a = b = c = 8.1140 Å and α = β = γ = 90° (JCPDS No. 01-073-1702). The diffraction peaks observed at 2θ values of 31.3°, 36.8°, 40.16°, 44.7°, 59.3°, and 66.1° correspond to the (220), (311), (222), (400), (511), and (440) reflection planes of NiCo$_2$O$_4$, respectively (Fig. 1a).$^{32}$ It can be seen that other peaks corresponding to hydroxide phases, namely, Ni(OH)$_2$ (00-059-0463) and Co(OH)$_2$ (00-002-1094), are still present owing to the incomplete conversion of the precursors into NiCo$_2$O$_4$, which resulted in
intermediate phases. However, the low intensity of most of these peaks suggests that these phases had an insignificant influence on the observed properties. Notably, the broad XRD diffraction peaks indicate the nanocrystallinity of the as-formed material. Fig. 1b and c show SEM images of a sample at different magnifications. The SEM images of the as-prepared sample reveal a rod-type morphology with an average diameter and length of ~9 nm and ~350 nm, respectively. Energy-dispersive X-ray (EDX) spectroscopy confirmed that the atomic ratio of Co to Ni was 1.97:1, which is consistent with the standard formula, i.e., NiCo$_2$O$_4$ (Fig. 1d). The oxidation states and surface chemical composition of NiCo$_2$O$_4$ nanorods were investigated by XPS. The XPS survey spectrum of NiCo$_2$O$_4$, as shown in Fig. 2a, suggests the presence of C, O, Ni, and Co elements as well as the absence of other impurity ions. The separate spectra of C 1s, O 1s, Ni 2p and Co 2p are presented in Fig. 2b–e. The high-resolution spectrum of the O 1s region shows an oxygen peak at 529.1 eV due to metal–oxygen bonds (Ni–O–Co), and the peak at 531.06 eV corresponds to surface defects or surface species such as hydroxyl groups and chemisorbed and lattice oxygen (Fig. 2c). Similarly, the Ni 2p spectrum exhibits two prominent spin–orbit peaks corresponding to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ at binding energies of 854.39 and 872 eV, respectively, with two shakeup satellite peaks, which are denoted as Sat. in the labeled graph (Fig. 2d). The Co 2p spectrum displays two major spin–orbit peaks corresponding to Co 2p$_{3/2}$ and Co 2p$_{1/2}$ at binding energies of 779.7 and 794.4 eV, respectively (Fig. 2e). These results show that the chemical composition of NiCo$_2$O$_4$ nanorods comprises Co$^{2+}$, Co$^{3+}$, Ni$^{2+}$, and Ni$^{3+}$, which is in close accordance with the literature on NiCo$_2$O$_4$ materials. The structural and crystalline characteristics of NiCo$_2$O$_4$ nanorods were further investigated via TEM and selected-area electron diffraction (SAED) studies.
Fig. 3a and b are TEM images of NiCo₂O₄ nanorods at different magnifications, which reveal a small diameter of ~8–11 nm with an average length of ~350 nm and indicate their large surface area, which is beneficial for the enhancement of performance in sensors, as well as pseudocapacitance. Fig. 3c is a magnified view of the circled area in Fig. 3b, which shows the interplanar spacings in Fig. 2 TEM images at (a) low magnification and (b) high magnification, (c) magnification of the circled area in (b) showing the interplanar spacing, (d) SAED pattern, and (e and f) percentage length and diameter distributions, respectively, of NiCo₂O₄ nanorods.
the marked region. Fig. 3d shows the SAED pattern, which indicates that the indexed diffraction rings are consistent with the XRD results. Fig. 3e and f show histograms of the percentage length and diameter distributions of NiCo₂O₄ nanorods, respectively, which were obtained from SEM images and further confirm that their length and diameter range between 100 and 600 nm and 4 and 14 nm, respectively. The N₂ adsorption/desorption isotherm was also obtained to reveal the porosity and surface area of as-formed NiCo₂O₄ nanorods. Fig. 4 shows the N₂ adsorption/desorption isotherm of NiCo₂O₄ nanorods and the corresponding Barrett–Joyner–Halenda (BJH) curve of pore size distribution (inset of Fig. 4), respectively. The type IV isotherm and type H3 hysteresis loop suggest that the nanorods are mesoporous in nature, with an average pore diameter, specific surface area and pore volume of 15.71 nm, 109.704 m² g⁻¹ and 0.603 cm³ g⁻¹, respectively. The formation of mesopores could be ascribed to the release of gas during the decomposition of the Ni–Co precursor, which was synthesized employing urea as a capping agent. This type of porosity with a large specific surface area and large pore volume is particularly favorable for sensors and supercapacitors, as it can facilitate charge transfer by shortening ion diffusion paths and provide more electroactive sites. The thermal behavior of hydrothermally produced NiCo₂O₄ nanorods was investigated by thermogravimetric analysis (TGA) at a scan rate of 5 °C min⁻¹ under an N₂ atmosphere up to 600 °C (Fig. 5). The weight loss (~5%) below 250 °C can be assigned to the dehydration of Ni–Co-based precursors. The second step (~13% weight loss) up to 400 °C in the TGA curve corresponds to the conversion of Ni–Co precursors into NiCo₂O₄ nanorods. Furthermore, no obvious weight loss was observed up to 600 °C, which indicated complete decomposition of the precursors and structural integrity. Hence, the high porosity that was generated can be related to the release of H₂O and CO₂ gases during the thermal decomposition/annealing step. Hence, the complete decomposition of the precursors gave rise to high porosity.

3.2. NNCOGCE as glucose sensor
The detection of glucose was performed by employing NNCOGCE as the working electrode in an electrochemical setup via three different techniques, namely, cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CA), using 0.1 M NaOH as the supporting solution (Scheme 2).

3.2.1. Electrocatalytic oxidation of glucose at the NNCOGCE. The electrochemical properties of the NNCOGCE for glucose sensors were investigated by CV in the potential window ranging from 0 to +0.6 V. As can be seen, in the absence of glucose the NNCOGCE generated higher current in comparison to the bare electrode and therefore exhibited better charge transfer capability (Fig. 6a). Furthermore, in the presence of glucose the NNCOGCE gave rise to a pair of redox peaks, which suggested the oxidation of glucose to gluconic acid with the subsequent generation of an electron (Fig. 6b). To clearly distinguish the redox peaks, the CV profile of the NNCOGCE at a scan rate of 5 mV s⁻¹ is shown separately in Fig. 6c, from which it can be seen that glucose is oxidized at around +0.4 V and transformed into gluconic acid, as observed by the increase in CV current at the oxidation peak. The oxidation potential of glucose was further confirmed by DPV testing, and a clear oxidation peak at +0.4 V was observed (Fig. 6d). The effect of the scan rate (5–40 mV s⁻¹) on the NNCOGCE in the presence of...
glucose was also observed (Fig. 6e), and it was noted that the current at the oxidation peak increased linearly with the square root of the scan rate, which suggested a diffusion-controlled process at the surface of the NNCOGCE (Fig. 6f). During the CV
scan, the redox reactions at the electrode were as follows (eqn (1) and (2)):

\[
\begin{align*}
\text{NiCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \leftrightarrow 2\text{CoOOH} + \text{NiOOH} + e^- \quad (1) \\
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (2)
\end{align*}
\]

At the working electrode, two processes occurred in the same anodic voltage range: the conversion of glucose into gluconolactone and the oxidation of Ni and Co ions, which each lost one electron to the solution (eqn (3) and (4)):

\[
\begin{align*}
\text{Ni(n)} + \text{Co(n)} & \rightarrow \text{Ni(i)} + \text{Co(m)} + 2e^- \quad (3) \\
\text{Glucose} & \rightarrow \text{Glucronolactone} + 2\text{H}^+ + 2e^- \quad (4)
\end{align*}
\]

These simultaneous oxidation processes caused the peak to appear on the addition of glucose at +0.4 V. However, the processes are largely dependent on the rate of oxidation of Ni(n) and Co(n) species. Hence, it can be assumed that the glucose-detecting ability is dependent on the intrinsic properties of NiCo$_2$O$_4$.

The CV profiles of the NNCOGCE were also recorded at different concentrations of injected glucose (Fig. 6g), and it was observed that the NNCOGCE exhibited a sensitive response to the injection of glucose and the current increased linearly with different added concentrations. A calibration plot of the induced current response against the concentration of injected glucose, as shown in Fig. 6h, gives a straight line, which highlights the potential of NiCo$_2$O$_4$ nanorods as a material for glucose sensors.

### 3.2.2. EIS analysis of the NNCOGCE for glucose sensors

The charge transfer capability of the NNCOGCE was further investigated by electrochemical impedance spectroscopy (EIS) studies. In EIS, at each excitation frequency the data that are obtained are usually expressed by Nyquist plots, in which the real impedance ($Z_\text{r}$) and imaginary impedance ($Z_\text{i}$) is plotted against the imaginary ($Z'_\text{r}$) and real ($Z'_\text{i}$), respectively. The impedance spectroscopy plots for the bare GCE and NNCOGCE are presented in Fig. 7a. An equivalent electrical model was designed on the basis of an adjusted interpretation of impedance behavior suggested by Jacobsen and West that takes into account diffusion impedances in cylindrical symmetry, which corresponds to a cylindrical rod dipped into a large volume of electrolyte. This assumption is closely correlated with the experimental setup used in the present work, in which the GCE and modified GCE had wire-like cylindrical shapes.

A magnified view of the high-frequency regions of the impedance spectra is shown in Fig. 7b, and it is seen that these graphs do not deviate from the behavior seen in Fig. 7a, which thus reconfirms the suitability of the aforementioned model for describing the behavior of this electrode.

The corresponding experimental circuit diagram is shown in Fig. 8. The distributed element $Z_d$ (which corresponds to the diffusion impedance) represents a particular case based on an infinite transmission line, in which the resistance decreases and the capacitance increases in proportion to the increase in the flow surface with distance from the electrode and the concentration is perturbed near the electrode surface as a result, which is represented by $\Delta c(x_0)$. The approximation of such a transmission line model to a lumped-parameters circuit is impractical, and hence a combination of empirical models and differential equations was used to model the impedance.

Here, $Z_d$ consists of both a resistive ($R_d$) and a capacitive ($C_d$) component, which are represented by the real and imaginary parts of the following equation, respectively:

\[
Z_d(s) = \sum \frac{\partial E}{\partial \Delta c_i} \frac{\partial c_i(s, x_0)}{i J_i(s, x_0)}
\]

where $s$ is the complex transform parameter, which has dimensions of frequency, $\partial E/\partial \Delta c_i$ is the partial derivative of the applied electric potential with respect to the concentration of the chemical species $i$, and $J$ is the flux density of the species.

The results of the fitting process are listed in Table 1. $R_d$ represents the charge transfer resistance of the material with respect to the electrochemical reaction, whereas $C_d$ is the...
double-layer capacitance. It is observed that $C_{dl}$ and $R_{ct}$ decreased upon the addition of glucose to the electrolyte, which corresponded to an increase in current, as seen in the amperometric response. The diffusion resistance and capacitance increased upon the addition of glucose, which was possibly because the electrochemical reaction caused the presence of ionized species in the vicinity of the electrode in the cell.

In comparison with the NNCOGCE, it was observed that the bare GCE was not sensitive at all to the analyte, and hence the charge transfer resistance was high and the $C_{dl}$ value was low, as no reaction occurred and hence no ionic species were present at the interface. The diffusion impedance as a whole remained high for the bare GCE, as the electronic characteristics of a bare GCE are not favorable for the conditions in the sensing experiment. These findings are consistent with the study by Shervedani et al., in which it was reported that the charge transfer resistance is dependent on the concentration of glucose for a material that is electrochemically sensitive to the presence of glucose in the electrolyte.\textsuperscript{50}

### 3.2.3. Amperometric detection of glucose by the NNCOGCE.

The electrochemical determination of glucose was further studied by chronoamperometry under conditions of continuous stirring in a 0.1 M NaOH solution by applying a fixed potential of +0.4 V.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bare GCE</th>
<th>NNCOGCE</th>
<th>NNCOGCE in presence of glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{ct}$ ($\Omega$)</td>
<td>$9.413 \times 10^4$</td>
<td>17.80</td>
<td>16.39</td>
</tr>
<tr>
<td>$C_{dl}$ (F)</td>
<td>$1.081 \times 10^{-9}$</td>
<td>1.29473</td>
<td>$1.35622 \times 10^{-7}$</td>
</tr>
<tr>
<td>$R_{d}$ ($\Omega$)</td>
<td>0.3763</td>
<td>$6.173 \times 10^3$</td>
<td>$3.433 \times 10^3$</td>
</tr>
<tr>
<td>$C_{d}$ (F)</td>
<td>4.15</td>
<td>$1.4548 \times 10^{-4}$</td>
<td>$8.68 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Fig. 9  
(a) Results of amperometric testing of the NNCOGCE on the injection of different concentrations of glucose in 0.1 M NaOH; magnifications of the plots for (i) low injected concentrations and (ii) higher injected concentrations are shown separately, (b) calibration plot of the concentration of injected glucose against the induced current response, (c) test results for the selectivity of the NNCOGCE for glucose in the presence of some common interfering species, namely, uric acid, dopamine, ascorbic acid, fructose, galactose, creatinine, acetaminophen and maltose, (d) results of repeatability test on the NNCOGCE with successive injections of 0.5 mM glucose, (e) results of long-term amperometric response test on the NNCOGCE with the injection of 50 $\mu$M glucose up to 4000 s.
Fig. 9a shows the amperometric response of the NNCOGCE upon successive injections of different concentrations of glucose. It can be seen that the NNCOGCE responded swiftly to glucose injections and achieved a steady-state current response within 3 s, which indicated a rapid and sensitive response. For better understanding, the amperometric response to glucose concentrations has been divided into two parts. Part (i) shows the current response for the addition of low concentrations of glucose and part (ii) shows the induced current response for the injection of higher concentrations of glucose. The overall current response was linearly proportional to the concentration of injected glucose, as can be seen in the corresponding calibration plot (Fig. 9b). Moreover, the NNCOGCE sensor displayed a linear response in the detection of glucose, with a wide dynamic linear range of 0.001–0.88 mM ($R^2 = 0.99057$), a notable detection limit of 63 nM and a high sensitivity of 4.710 $\mu$A $\text{mM}^{-1}$ $\text{cm}^{-2}$. The remarkable sensing performance can be ascribed to the large surface area and suitable pore size of NiCo$_2$O$_4$ nanorods, which accelerated the charge transfer process by shortening the ion diffusion paths.

### 3.2.4. Selectivity tests

Selectivity is also an important attribute for non-enzymatic electrochemical glucose sensors. The selectivity of the NNCOGCE for glucose was tested in the presence of some potentially interfering species, namely, uric acid, dopamine, ascorbic acid, fructose, galactose, creatinine, acetonilophen and maltose, which are usually present in blood together with glucose. Although these interferents are present at low concentrations in blood (30 times less than that of glucose), they have a significant effect on the glucose detection process. Therefore, the amperometric response of the NNCOGCE was tested in 0.1 M NaOH solution at an applied potential of +0.4 V upon successive additions of different concentrations of glucose and a threefold excess of each interfering species (uric acid, ascorbic acid, dopamine, fructose, galactose, creatinine, acetonilophen and maltose). Well-defined and sensitive responses were observed for successive additions of glucose, and no noteworthy responses were observed for any of the interfering species (Fig. 9c). The resistance to interference of the NNCOGCE can be attributed to the positive synergism between NNCOGCE and glucose, which enables enhanced charge transfer efficiency. Furthermore, the negatively charged Nafion membrane present over the NNCOGCE also plays a minor role in providing enhanced selectivity by repellling interfering agents such as uric acid and ascorbic acid. Hence, the NNCOGCE is selective for glucose.$^{7,12–25}$

#### 3.2.5. Repeatability, stability and storage stability tests

The repeatability of the NNCOGCE was also investigated by repeating the amperometric test after successive injections of 0.5 mM glucose. It can be seen from Fig. 9d that the induced current response of the NNCOGCE remained stable with negligible variations even after six consecutive injections of glucose, which confirmed the repeatability of the sensor. The operational stability of the NNCOGCE was also determined by continuous amperometric $i$-$t$ curve analysis. The amperometric response of the present sensor retained $\sim 97\%$ of its initial value after continuous analysis for up to 4000 s, which highlighted the stability of the NNCOGCE (Fig. 9e). The high storage stability of the NNCOGCE was also tested by keeping modified GCEs in air-tight desiccators, and the amperometric responses were measured after a period of 15 days. The electrodes did not display any noteworthy deviation, which confirmed the robustness of the NNCOGCE. Moreover, this test also indicates that these electrodes can be redesigned and a large array of similar electrodes (NNCOGCE) with the same current response can be fabricated.

#### 3.2.6. Real sample analysis

The NNCOGCE was further investigated for the determination of glucose levels in a real sample, namely, human serum (provided by a local diagnostic laboratory), using the standard addition method. In a series of experiments, two samples were spiked with specific glucose levels (uric acid, dopamine, ascorbic acid, fructose, galactose, creatinine, acetonilophen and maltose). Well-defined and sensitive responses were observed for successive additions of glucose, and no noteworthy responses were observed for any of the interfering species (Fig. 9c). The resistance to interference of the NNCOGCE can be attributed to the positive synergism between NNCOGCE and glucose, which enables enhanced charge transfer efficiency. Furthermore, the negatively charged Nafion membrane present over the NNCOGCE also plays a minor role in providing enhanced selectivity by repellling interfering agents such as uric acid and ascorbic acid. Hence, the NNCOGCE is selective for glucose.$^{7,12–25}$

<table>
<thead>
<tr>
<th>Material</th>
<th>Detection limit ($\mu$M)</th>
<th>Linear range (mM)</th>
<th>Sensitivity ($\mu$A $\text{mM}^{-1}$ $\text{cm}^{-2}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flower-like copper cobaltite nanosheets on graphite paper</td>
<td>5</td>
<td>Up to 0.32</td>
<td>3625</td>
<td>1</td>
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<tr>
<td>Sucrose-templated copper oxide microspheres</td>
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<td>2–9</td>
<td>26.59</td>
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<td>Au nanoparticles-functionalyzed 3D hierarchical ZnO nanostructures</td>
<td>20</td>
<td>1–20</td>
<td>1.409</td>
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<td>Nanoneedle-like copper oxide on N-doped reduced graphene oxide</td>
<td>0.01</td>
<td>0.0005–0.639</td>
<td>3.4</td>
<td>9</td>
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<td>Ultrathin graphite-like carbon nitride/WO$_3$, semiconductor nanoheterostructures</td>
<td>0.1</td>
<td>0.01–7.12</td>
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<td>10</td>
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<tr>
<td>Copper nanoparticles dispersed in graphene-ferrocene redox polymer</td>
<td>160</td>
<td>0.50–15</td>
<td>14.3</td>
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<tr>
<td>Pt$_3$Ru$_1$ alloy nanoparticles</td>
<td>0.3</td>
<td>0.050–10</td>
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<td>Ag nanoparticles on functionalized carbon nanotubes</td>
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<td>Cobalt oxide/Au/FTO hierarchical nanostructure</td>
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<td>6000</td>
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<td>3D Ni$_3$P nanoarray</td>
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<td>0.001–3</td>
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<tr>
<td>Cu$_2$O on AlOOH/reduced graphene oxide</td>
<td>2.6</td>
<td>0.005–14.77</td>
<td>155.1</td>
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<td>Ni(OH)$_2$-decorated sulfur-doped carbon nanoparticles</td>
<td>0.028</td>
<td>0.0001–5.22 and 5.22–10.22</td>
<td>3800 and 1297</td>
<td>18</td>
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<td>Cu/Cu$_2$O nanohybrid electrocatalyst</td>
<td>1.6</td>
<td>Up to 40</td>
<td>1344.12</td>
<td>19</td>
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<td>3D rambutan-like CuO and CuO/reduced graphene oxide</td>
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<td>0.0005–3.75</td>
<td>52.1</td>
<td>20</td>
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<td>CoWO$_4$ nanospheres</td>
<td>0.7</td>
<td>0.00005–4.5</td>
<td>1416.2</td>
<td>21</td>
</tr>
<tr>
<td>Porous NiO/Co$_2$O$_3$ hybrid nanoflake arrays</td>
<td>1</td>
<td>0.001–2.9</td>
<td>154.4</td>
<td>22</td>
</tr>
<tr>
<td>Hierarchical 3-dimensional nickel-iron nanosheet arrays on carbon fiber paper</td>
<td>0.031</td>
<td>0.0005–0.2</td>
<td>7900</td>
<td>23</td>
</tr>
<tr>
<td>TiO$_2$-decorated Co$_3$O$_4$ acicular nanotube arrays</td>
<td>0.3396</td>
<td>Up to 3</td>
<td>2008.82</td>
<td>24</td>
</tr>
<tr>
<td>Co$_3$O$_4$ nanoflowers and 3D graphene oxide hydrogel</td>
<td>—</td>
<td>0.25–10</td>
<td>492.8</td>
<td>25</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ nanorods</td>
<td>0.063</td>
<td>0.001–0.88</td>
<td>4710</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Table 2** Comparison of NNCOGCE-based glucose sensor with other recently reported glucose sensors.
concentrations, and on the basis of repeated responses ($n = 3$) the concentrations of glucose were determined with good recoveries, as summarized in Table S1 (ESI†). The results validate the suitability of the proposed sensor (NNCOGCE) for real sample analysis.

The sensing performance of the NNCOGCE, together with that of some recently reported glucose sensors, is listed in Table 2, from which it can be concluded that the NNCOGCE has advantages with respect to other reported glucose sensors. Moreover, its remarkable performance, in particular in the absence of any conducting material (e.g., graphene, CNTs, etc.), highlights the potential of the NNCOGCE as a candidate for glucose sensors in preference to other sensors.

### 3.3. NNCOGCE as supercapacitor

The supercapacitor properties of the NNCOGCE were investigated via cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) studies in the potential window of $-0.1$ to $+0.5$ V using a $1$ M KOH solution (Fig. 10). A general scheme of NiCo$_2$O$_4$ nanorods-based supercapacitors is presented in Scheme 3.

![CV profile of the NNCOGCE at a scan rate of 25 mV s$^{-1}$ in 1 M KOH.](image1)

![CV profiles of the NNCOGCE at different scan rates of 25–300 mV s$^{-1}$.](image2)

![Charge–discharge profile of the NNCOGCE at a current density of 2 A g$^{-1}$.](image3)

![Charge–discharge profiles of the NNCOGCE at different current densities of 2–20 A g$^{-1}$.](image4)

![Plot of current density against specific capacitance.](image5)

![Ragone plot for the NNCOGCE.](image6)
3.3.1. Electrochemical properties of the NNCOGCE for supercapacitors. The electrochemical properties of the NNCOGCE were initially examined by CV at different scan rates (25–300 mV s⁻¹). A comparison of the CV profiles of the bare GCE and NNCOGCE at a scan rate of 25 mV s⁻¹ is shown in Fig. S1 (ESI†). It can be seen that the CV integrated area for the NNCOGCE increased remarkably in comparison with that for the bare GCE owing to the perfect synergy between NiCo₂O₄ nanorods and the alkaline electrolyte, which indicated a noteworthy increase in specific capacitance. The increase in specific capacitance can be attributed to the large surface area and suitable pore size and pore volume of NiCo₂O₄ nanorods, which provide short diffusion paths for OH⁻ ions to the interior surface of the electrode and result in an increase in current, as is visible in the CV profiles. The CV profile for the NNCOGCE at a scan rate of 25 mV s⁻¹ is shown separately in Fig. 10a. The shape of the CV curve clearly shows a well-defined pair of redox peaks, which reveal its pseudocapacitive nature. These peaks correspond to the reversible faradaic redox reactions of Ni²⁺/Ni³⁺ and Co³⁺/Co⁴⁺ transitions. These redox reactions can be expressed by the following equations:

\[ \text{NiCo}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow \text{NiO}_2\text{H} + 2\text{CoO}_2\text{H} + e^- \]

\[ \text{CoO}_2\text{H} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \]

The CV profiles at different scan rates (25–300 mV s⁻¹) are also presented in Fig. 10b, which suggests that the area under the CV curve increased directly with an increase in the scan rate for the NNCOGCE. It was also observed that the shape of the CV curves for the NNCOGCE was maintained without any distortion even at a higher scan rate of 300 mV s⁻¹, which demonstrated its high rate performance.³

3.3.2. Galvanostatic charge-discharge (GCD) studies. GCD measurements were also performed in the potential window of −0.1 to +0.5 V to confirm the pseudocapacitive nature of the NNCOGCE. The GCD profile of the NNCOGCE at a current density of 2 A g⁻¹ is presented in Fig. 10c, which clearly shows a non-linear charge-discharge curve. The non-linear charge-discharge curves at different current densities (2–20 A g⁻¹) confirm the pseudocapacitive behavior of the NNCOGCE (Fig. 10d).

The specific capacitance of the NNCOGCE was calculated to be 980 F g⁻¹ at a current density of 2 A g⁻¹. The calculated specific capacitance is plotted against the current density in Fig. 10e. The specific capacitance of the NNCOGCE was calculated to be 980, 865, 758.33, 750, 735, 720, 705, 700, 650, and 600 F g⁻¹ at constant current densities of 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, and 20 A g⁻¹, respectively, which demonstrates that the specific capacitance decreased on an increase in the current density. The process used to calculate the specific capacitance is given in the ESI.† It can be associated with the fact that at higher current densities very few electrolyte ions can occupy the inner spaces of the electrode.³,²¹,²² High capacitance retention rates and rate performance were also observed for the NNCOGCE, as it retained 71.42% and 61.22% of its initial capacitance at higher current densities of 10 and 20 A g⁻¹, respectively. The superior electrochemical properties can be assigned to the following reasons: (i) the large surface area of NiCo₂O₄ nanorods (109.704 m² g⁻¹) contributes immensely to the achievement of high charge storage efficiency; (ii) the large pore size (15.71 nm) and pore volume (0.603 cm³ g⁻¹) of NiCo₂O₄ nanorods provide ion-buffering reservoirs for OH⁻ ions, which provide short ion diffusion paths to the interior surfaces of the electrode and ultimately accelerate the kinetic process of the diffusion of OH⁻ ions in the NNCOGCE, which thus enhances its electrochemical performance; (iii) the short ion diffusion pathways lead to high specific capacitance and accelerated electrochemical kinetics; and (iv) fascinating features such as the high electronic conductivity and electrochemical activity of NiCo₂O₄ nanorods improve the electrochemical performance of the NNCOGCE. A Ragone plot is also presented in Fig. 10f, which highlights the remarkable rate performance of the NNCOGCE and shows that the energy density decreased and the power density increased on an increase in the current density. The maximum energy density and power density of the NNCOGCE were calculated to be 49 Wh kg⁻¹ and 3000 W kg⁻¹, respectively. The cycling stability and cycle life of the NNCOGCE were also determined by repeating 1000 charge−discharge cycles at a constant current density of 10 A g⁻¹, as shown in Fig. 11. It can be observed that the NNCOGCE retained 92% of its initial specific capacitance even after 1000 cycles. The Nafion film also played a minor role in delivering high Coulombic efficiency.

Scheme 3 Schematic diagram of NiCo₂O₄ nanorods-based supercapacitor.
efficiency by providing adhesive properties to the nanorods on the GCE surface. The first 10 charge–discharge cycles are shown in the inset of Fig. 11, from which it can be concluded that the NNCOGCE displayed excellent cycling efficiency. The excellent cycling stability can also be ascribed to the fact that during the charge–discharge process the unique pore structure of NiCo₂O₄ nanorods is believed to buffer possible volume changes during the insertion/extraction process of OH⁻/CO₃²⁻ ions.

3.3.3. EIS analysis of the NNCOGCE for supercapacitors. The supercapacitor properties of the fabricated electrode were further studied electrochemically by EIS. The impedance spectroscopy plots for the bare GCE and NNCOGCE in 1 M KOH are presented in Fig. 12a, and the high-frequency portions are specifically magnified in Fig. 12b. The impedance data were fitted according to an electrical model of porous electrodes presented by Fletcher, which was initially developed for conducting polymers but was accordingly adapted to the current material. The circuit model consists of a discrete ladder network, which accounts for the ionic and electronic resistances, as well as contributions to the resistance and capacitance from faradaic and dielectric components.

On the basis of the model described by Fletcher, a schematic diagram of the equivalent circuit is presented in Fig. 13. In the circuit diagram, \( R_e \) and \( R_i \) represent the electronic and ionic resistances, respectively, whereas \( C_f \) represents the capacitance due to “fast”, or frequency-independent, capacitances (which correspond to pseudocapacitance), and \( C_p \) represents the capacitance due to “slow”, or frequency-dependent, capacitances (which correspond to double-layer or dielectric capacitance). \( R_{ct} \) represents the charge transfer resistance of the material with respect to oxidation/reduction processes of localized states. \( R_{ct}, C_f, \) and \( C_p \) together constitute the interphase impedance at the interface of the material and the electrolyte. The modifications to the initial model proposed by Fletcher take into account the facts that semiconductors and carbon-based materials are generally better conductors with higher structural order than conducting polymers and that the supercapacitor applications in this study are generally used at low to medium frequencies (0.1 Hz to 100 kHz). The function governing the impedance is given below:

\[
Z(s) = \left(1 + \frac{\tanh(\mu(s))}{\mu(s)}\right) \frac{R_e R_{ct}}{R_i + R_e} + \sqrt{(R_i + R_e)Z_s(s) \coth(2\mu(s))}
\]

where

\[
Z_s(s) = \frac{1}{C_{dl} s + \frac{1}{R_{ct} + \frac{1}{\mu(s)}}}
\]

\[
\mu(s) = \sqrt{\frac{R_i + R_e}{4Z_s(s)}}
\]

The results of fitting based on the model described above for the bare GCE and NNCOGCE are presented in Table 3. Several observations can be made from this table. Firstly, it was found that the ionic resistance decreased and the electronic resistance increased after the GCE was modified with NiCo₂O₄. This was attributed to the higher porosity and larger pore size of NiCo₂O₄, as the GCE has negligible porosity. Secondly, the charge transfer resistance \( R_{ct} \) increased for the NNCOGCE in comparison with the bare GCE. This is consistent with the study by Yang et al., which concluded that the charge transfer resistance increases with the electronic resistance. A high value of charge transfer resistance greatly limits the ability of a material to function as a double-layer capacitor, and hence the greatest increase in capacitance was observed for \( C_f \), i.e., the faradaic component (or pseudocapacitance) when the GCE was...
modified with NiCo$_2$O$_4$. The EIS results thus support the theory that a strong faradaic reaction contributed to the significant capacitive properties of the material.

A comparative table has been constructed to summarize the supercapacitor performance of some electrode materials based on NiCo$_2$O$_4$ (Table 4). It can be concluded that Nafion-supported NiCo$_2$O$_4$ nanorods, as presented in this work, can also be a potential candidate for next-generation energy storage devices. The results are superior to those of many earlier reports and comparable to those of few other reports. Moreover, the remarkable performance of the NNCOGCE in the absence of any conducting material (e.g., CNTs, rGO, etc.) as a composite and the incorporation of an electrode with a very small diameter (3 mm) strengthen its advantages over other electrodes.

### 4. Conclusion

In summary, a simple two-step method was employed for the fabrication of multifunctional NiCo$_2$O$_4$ nanorods. The fabricated nanorods were then assembled on the working area of a glassy carbon electrode with the use of Nafion, and the as-formed modified electrode (Nafion/NCO/GCE or NNCOGCE) was employed as a working electrode in both a glucose sensor and a pseudocapacitor. The NNCOGCE selectively detected glucose very rapidly (3 s) over a wide linear range (0.001–0.88 mM) with high sensitivity (4.710 mA mM$^{-1}$/Ccm$^{-2}$) and a low LOD (63 nM). Furthermore, the NNCOGCE delivered a high specific capacitance (980 F g$^{-1}$ at 2 A g$^{-1}$) with excellent rate performance (retention of 71.42% at 10 A g$^{-1}$) and cycling stability (retention of 92% up to 1000 cycles). Its good response as a glucose sensor and supercapacitor can be attributed to the noteworthy large surface area, suitable pore size and volume, and superior conductivity of NiCo$_2$O$_4$ nanorods. The present

### Table 3  Circuit parameters determined for the given equivalent circuit

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bare GCE</th>
<th>NNCOGCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_\text{ct}$ (Ω)</td>
<td>$3.09 \times 10^{-15}$</td>
<td>$4.489 \times 10^7$</td>
</tr>
<tr>
<td>$C_\text{f}$ (F)</td>
<td>$4.3572 \times 10^{-14}$</td>
<td>$1.71 \times 10^{-4}$</td>
</tr>
<tr>
<td>$C_\text{p}$ (F)</td>
<td>$6.6481 \times 10^{-4}$</td>
<td>$7.401 \times 10^{-4}$</td>
</tr>
<tr>
<td>$R_\text{e}$ (Ω)</td>
<td>0.46628</td>
<td>3.505</td>
</tr>
<tr>
<td>$R_\text{i}$ (Ω)</td>
<td>$2.224 \times 10^4$</td>
<td>$4.018 \times 10^4$</td>
</tr>
</tbody>
</table>

### Table 4  Comparison of NNCOGCE-based supercapacitor with other reported supercapacitors based on NiCo$_2$O$_4$

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrode used</th>
<th>Electrolyte medium</th>
<th>Specific capacitance (F g$^{-1}$)</th>
<th>Current density (A g$^{-1}$)</th>
<th>Retention of specific capacitance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCo$_2$O$_4$ nanorods</td>
<td>Ni foam</td>
<td>2 M KOH</td>
<td>758</td>
<td>1</td>
<td>80% after 1500 cycles</td>
<td>31</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ nanorods</td>
<td>Ni foam</td>
<td>2 M KOH</td>
<td>565</td>
<td>1</td>
<td>77.6% after 1000 cycles</td>
<td>32</td>
</tr>
<tr>
<td>Ni foam-supported ultrathin mesoporous NiCo$_2$O$_4$ nanosheets</td>
<td>Ni foam (1 cm × 1 cm)</td>
<td>3 M KOH</td>
<td>2010</td>
<td>2</td>
<td>—</td>
<td>54</td>
</tr>
<tr>
<td>CNF@NiCo$_2$O$_4$ nanosheet</td>
<td>Ni foam</td>
<td>2 M KOH</td>
<td>902</td>
<td>2</td>
<td>91.23% after 2000 cycles</td>
<td>55</td>
</tr>
<tr>
<td>Porous NiCo$_2$O$_4$ nanosheet arrays</td>
<td>Carbon fabric</td>
<td>3 M KOH</td>
<td>2658</td>
<td>2</td>
<td>80% after 3000 cycles</td>
<td>56</td>
</tr>
<tr>
<td>Hierarchical NiCo$_2$O$_4$ nanosheets</td>
<td>Ni foam</td>
<td>6 M KOH</td>
<td>899</td>
<td>1</td>
<td>84.9% after 6000 cycles</td>
<td>57</td>
</tr>
<tr>
<td>Mesoporous NiCo$_2$O$_4$ nanosheets</td>
<td>Ni foam</td>
<td>2 M KOH</td>
<td>400</td>
<td>20</td>
<td>95.2% after 5000 cycles</td>
<td>58</td>
</tr>
<tr>
<td>Hierarchical porous NiCo$_2$O$_4$ nanowires</td>
<td>Graphite paper (1 cm$^2$)</td>
<td>1 M KOH</td>
<td>743</td>
<td>1</td>
<td>93.8% after 3000 cycles</td>
<td>59</td>
</tr>
<tr>
<td>3D hierarchical flower-shaped NiCo$_2$O$_4$ microsphere</td>
<td>Ni foam (1 cm × 1 cm)</td>
<td>6 M KOH</td>
<td>1006</td>
<td>1</td>
<td>93.2% after 1000 cycles</td>
<td>60</td>
</tr>
<tr>
<td>Chain-like NiCo$_2$O$_4$ nanowires</td>
<td>Ni foam</td>
<td>6 M KOH</td>
<td>1284</td>
<td>2</td>
<td>97.5% after 3000 cycles</td>
<td>61</td>
</tr>
<tr>
<td>Mesoporous NiCo$_2$O$_4$ nanospheres</td>
<td>Ni foam (1 cm × 1 cm)</td>
<td>6 M KOH</td>
<td>842</td>
<td>2</td>
<td>103% after 5000 cycles</td>
<td>62</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ nanorods</td>
<td>GCE (3 mm diameter)</td>
<td>1 M KOH</td>
<td>980</td>
<td>2</td>
<td>92% after 1000 cycles</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Fig. 13  Schematic diagram of electrode in solution for supercapacitor test (with equivalent circuit used to fit the EIS data).
work is of significance, because the facile preparation of multifunctional NiCo$_2$O$_4$ nanorods may facilitate successful real-world applications, in particular in the development of glucose sensors and supercapacitors, as well as multifunctional nanomaterials for use in integrated devices.

Conflicts of interest
There are no conflicts of interest to declare.

Acknowledgements
The authors thank the Sophisticated Instrumentation Centre (SIC), IIT Indore for providing the characterization facilities. S. M. M. thanks SERB-DST (Project No. EMR/2016/001113), New Delhi for a research grant and IIT Indore for funding. We sincerely acknowledge ACMS, IIT Kanpur for providing the XPS facility. We are grateful to Prof. G. Hundal and Dr Sanyog Sharma for helpful discussions. M. S. thanks SERB-DST (Project No. EMR/2016/001113), New Delhi, India for providing research fellowships.

References