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Chemical deposition and exfoliation from liquid crystal template: Nickel/nickel (II) hydroxide nanoflakes electrocatalyst for a non-enzymatic glucose oxidation reaction



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KEYWORDS

Nickel hydroxide; Nanoflakes; Liquid crystal template; Glucose oxidation **Abstract** This work reports the synthesis of nickel/nickel hydroxides nanoflakes (Ni/Ni(OH)₂-NFs) at room temperature via a novel chemical deposition and exfoliation from a liquid crystal template mixture. The nickel ions dissolved in the interstitial aqueous domain of the Brij®78 hexagonal liquid crystal template were deposited by a reducing agent of sodium borohydride that concurrently reduces the nickel ions and generates extreme hydrogen gas bubbles, that exfoliated the nickel/nickel hydroxide layers. The Ni/Ni(OH)₂-NFs crystal structure, morphology, and surface area characterizations revealed the formation of semi-crystalline α -Ni(OH)₂ nonflakes with a thickness of approximately 10 nm and a specific surface area of about 135 m²/g. The electrochemical measurements of cyclic voltammetry, chronoamperometry, and impedance analysis showed that the Ni/Ni(OH)₂-NFs exhibited significant performance for the glucose non-enzymatic oxidation in an alkaline solution in comparison to the *bare*-nickel hydroxide (*bare*-Ni(OH)₂) deposited without surfactant. The Ni/Ni(OH)₂-NFs electrode showed superior glucose oxidation activity over the *bare*-Ni(OH)₂ catalyst with a sensitivity of 1.078 mA mM⁻¹ cm⁻² with a linear concentration dependency range from 0.2 to 60 mM and a detection limit of 0.2 mM (S/N = 3). The enhanced

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1878-5352 © 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). electrochemical active surface area and mesoporosity of the 2D nanoflakes make the Ni/Ni(OH)₂-NFs a promising catalyst in the application of glucose non-enzymatic sensing.

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1. Introduction

Glucose detection is very important not only in the field of clinical biochemistry but also in food processing and environmental monitoring (Xia et al., 2017; Heyser et al., 2019; Shabnam et al., 2017; Shervedani et al., 2014). To date, numerous approaches have been successfully used for glucose determination, such as fluorescence (Chen et al., 2017), chemiluminescence (Li et al., 2019), spectrometry (Galant et al., 2015), and electrochemical methods (Zhu et al., 2018; Lu et al., 2015b). Among these techniques, electrochemical glucose sensors have attracted the attention of scientists because of the important properties of their detection method, such as sensitivity, rapid response time, simplicity, and low production cost (Rajendran et al., 2018; Huang et al., 2017).

In general, glucose sensors are enzyme- and non-enzyme-based sensors (Mao et al., 2021; Hovancová et al., 2020; Kailasa et al., 2020). The glucose-enzymatic sensors rely on the immobilized oxidase of glucose on a variety of supports, which results in high sensitivity and selectivity. However, these glucose sensing platforms suffer from the disadvantages of complicated immobilization procedures, expensive and chemical instability (Devasenathipathy et al., 2015; Márquez et al., 2017). Therefore, the development and advances of the nonenzymatic glucose sensors with high stability, selectivity, sensitivity, are emerging (Tekacharin et al., 2018; Yang et al., 2016). Transition metal hydroxides and metal oxides such as Co_3O_4 (Mahmoudian et al., 2016), MnO₂ (Hao et al., 2020), NiO (Heyser et al., 2019; Ci et al., 2014), and Ni(OH)₂ (Mao et al., 2019; Tian et al., 2018) were widely considered to be alternatives to non-enzymatic glucose sensors.

Among the transition metal compounds, the nanostructures of Ni (OH)2 with various morphologies such as nanoparticles, nanowires, nanoflakes, nanosheets, and microspheres have been used as an ideal catalyst for glucose oxidation because they have high electrocatalytic activity, are environmentally friendly, and are very economic (Xiao et al., 2017; Wang et al., 2011; Fan et al., 2014). Further, nickel hydroxide with the well-known polymorphs of α - and β -Ni(OH)₂ (Wang et al., 2013; Tong et al., 2012; Kovalenko and Kotok, 2019) has a typical structure of hexagonal layered crystals and therefore makes it easy to synthesize electrochemically active 2D nanoflakes with a very high surface (Huang et al., 2017) for a wide range of applications in electrocatalyst and sensor platforms (Wang et al., 2018; Zhou et al., 2017; Yang et al., 2019). The 2D nanoflakes have the advantages of a high surface area with an interstitial mesoporous structure that acts as an open channel to facilitate the diffusion of the analytes in the sensing architecture (Xia et al., 2017; Wang et al., 2013; Zhu et al., 2014). Recently, a conductive Ni-based metal-organic framework nanosheet arrays (Ni-MOF) having aminotriphenylene hydrochloride or exahydroxytriphenylene ligands were shown highperformance for glucose oxidation catalyst with sensitivity reach up to of 21.744 mA mA/mM cm² in concentration range of 0.001 to 8 mM glucose and detection limit of 0.57 µM (Qiao, et al., 2020a, 2020b; Lu and Wu, 2018). However, the linear detection range of the glucose oxidation was limited within the range of 0.001-8 mM which restricted the use of the Ni-MOF catalyst for the determination of higher glucose concentration.

Several methods have been proposed to prepare nanostructure Ni (OH)₂, including hydrothermal synthesis (Huang et al., 2017; Hutton et al., 2011), electrochemical deposition (Lang et al., 2009), and chemical precipitation (Lai et al., 2020). In the chemical method, the material nanostructure features can be controlled through numerous factors such as the preparation temperature, solvents, reactant concentration,

and surfactant templates (Tientong et al., 2014; Ren et al., 2012). Nevertheless, the template approach based on the surfactant soft template is still the most popular and effective technique for the synthesis of high-surface-area mesoporous transition metal compounds (Zhao et al., 2007). Using this approach, Zhao et al. (2008) reported the electrochemical deposition of mesoporous nickel hydroxide and nickel oxide electrodes from the hexagonal liquid crystalline phase of surfactant Brij®56, which yielded high surface areas and controlled mesostructures. The specific capacitance of the produced mesoporous electrodes reached 578 F/g, which is related to the mesoporous structures and high specific surface area. In a relevant work, Ghanem et al. (Ghanem et al., 2015; Ghanem et al., 2017) reported a new synthesis approach for 2D mesoporous Ni/Ni(OH)2 nanoflakes via the chemical deposition of nickel ions dissolved in the lyotropic surfactant interstitial aqueous domain. The chemical reduction of nickel ions was performed by using an excess of sodium borohydride solution, which in turn generated concurrent hydrogen bubbles that exfoliated the Ni/Ni(OH)₂ interstitial layers deposited within the surfactant template mixture. The obtained Ni/Ni(OH)2 nanoflakes showed significant electrocatalytic oxidation activity for both urea and ethanol in an alkaline solution in contrast to the bare-Ni/Ni(OH)2 deposited without surfactant. The activity enhancement was credited to the considerable increase in the catalyst surface area as a result of nano-structuring the Ni/Ni(OH)2 to the 2D nanoflake framework. However, the chemical reduction of the nickel template mixture was performed in the bulk form (in a glass vial), which resulted in the non-uniform deposition of nanoflakes. The present work demonstrates a novel and facile approach to prepare 2D Ni/Ni(OH)2 nanoflakes by using the chemical deposition and in-situe exfoliation from a template of nickel surfactant liquid crystal (LCT) mixture at room temperature. Firstly, the nickel LCT mixture was self-assembled as a thin layer in a Petri dish, followed by the addition of excess NaBH₄ solution, which reduced the nickel ions in the aqueous domain of LCT and produced hydrogen bubbles that simultaneously exfoliated the deposited Ni/Ni(OH)2 nano-layers. The physicochemical identification of the Ni/Ni(OH)2 nanoflake surface morphology and crystal structure was conducted using X-ray diffraction, N2 adsorption-desorption isotherm, and scanning and transmission electron microscopy. The Ni/Ni(OH)2 nanoflakes' electrochemical sensing performance was examined for glucose oxidation in an alkaline solution by electrochemical and impedance techniques and evaluated against the bare-Ni/Ni(OH)2 deposited without surfactant and to the state-of-the-art nickel-based catalysts reported in the literature.

2. Experimental

2.1. Materials and chemicals

Nickel acetate tetrahydrate Ni(COOH₃)₂·4H₂O, polyethylene glycol octadecyl ether Brij@78 ($C_{18}H_{37}(OCH_2CH_2)_{20}OH$), Nafion (5% in a mixture of lower aliphatic alcohols and water), glucose, ascorbic acid (AA), uric acid (UA), sodium chloride (NaCl) and sodium borohydride, NaBH₄, were purchased from Sigma Aldrich (USA). Pure potassium hydroxide pellets (KOH, 85%) were obtained from AnalaR (USA). Isopropanol was procured from the WINLAB company for laboratory chemicals (>99%). All the chemicals were of analytical grade and used without any further purification.



Scheme 1 Chemical deposition and exfoliation scheme of Ni/Ni(OH)₂ nanoflakes at 25 °C.

All the solutions were prepared with deionized water (18.2 M Ω) obtained from Milli-Q ultrapure water purification system.

2.2. Synthesis of Ni/Ni(OH)₂ nanoflakes

The preparation of Ni/Ni(OH)2 nanoflakes (Ni/Ni(OH)2-NFs) was carried out as shown in Scheme 1 by the self-assembly of the nickel liquid template (Ni-LCT) mixture in a Petri dish. Firstly, the nickel-template mixture was prepared by the physical mixing of 2.0 g of melted non-ionic Brij®78 surfactant, 5.0 g of nickel acetate solution (0.5 M), and 5.0 g of deionized water. The template mixture was mixed using an ultrasonic probe until a homogenous solution was obtained. Then, the Petri dish with the template mixture was left in an open atmosphere at 25 \pm 1 °C to evaporate water until the ratio of the surfactant to water reached 40%; this corresponded to the hexagonal phase of the liquid crystal template. Then, an excess of sodium borohydride (NaBH₄, 1.0 M) reducing agent solution was sprayed over the hexagonal nickel template mixture in the Petri dish. As shown in Scheme 1, upon the addition of NaBH₄, an effervescence of hydrogen bubbles started to rise and the template mixture turned to black, indicating the commence of the nanoflake deposition from the lyotropic surfactant mixture. The mixture was left overnight until the reduction process was completed, and the precipitate was washed 4-5 times by heated distilled water (50 °C) and stirring to remove the surfactant. Finally, the precipitate was recovered by centrifugation and dried in an oven overnight at 50 °C. The non-porous nickel hydroxide (bare-Ni(OH)₂) was obtained by the chemical reduction of aqueous nickel solution with a solution of NaBH₄ reducing agent (1.0 M) and the absence of the surfactant Brij®78.

2.3. Characterisations of Ni/Ni(OH)₂ nanoflakes

The surface morphology and fine structure of the Ni/Ni(OH)₂ nanoflakes and *bare*-Ni(OH)₂ were executed using scanning (SEM, JSM-7600F; JEOL) and transmission electron microscope (TEM, JEM 2100F-JEOL, Tokyo, Japan), and the X-ray diffraction (XRD) analysis of the as-synthesized catalyst was carried out using a D2 Phaser X-ray diffractometer (Bruker, Germany) having Cu K_{α} radiation ($\lambda = 1.5418$ Å). The

specific surface area of the $Ni/Ni(OH)_2$ nanoflakes was performed using a V-Sorb 2800 Porosimetry Analyzer via Brunauer-Emmer-Teller (BET) method.

The electrochemical characterizations of cyclic voltammetry (CV), chronoamperometry, and impedance analysis were performed using Potentiostatic Galvanostat (Metrohm Auto-Lab Potentiostatic Machine: PGSTAT302N). All the electrochemical measurements were carried out using a threeelectrode electrochemical cell using Ag/AgCl and a platinum sheet (0.5 cm \times 0.5 cm) as the reference and the counter electrode, respectively. A carbon paper (CP, 1.0 cm \times 1.0 cm, Sigracetr, grade GDL-24BC, SGL) loaded with the catalyst ink was used as a working electrode in the KOH electrolyte. The ink of the Ni/Ni(OH)₂ nanoflakes for the electrochemical characterization was obtained by sonicating 10 mg of the catalyst, 10 µL of Nafion, 0.5 mL of deionized water, and 0.5 mL of isopropanol for 30 min. in a glass vial using an ultrasonication probe. To obtain the working electrode, a known volume of the catalyst ink was physically cast onto one face of the carbon paper followed by drying in a hot airflow in an open atmosphere, and all the measured current was normalized to the electrode geometric area of 1.0 cm². In addition, all the electrochemical measurements related to glucose oxidation have been reproduced at least three times during the same time and less than 2.0% relative standard deviation was obtained.

3. Results and discussion

3.1. Ni/Ni(OH) 2 nanoflakes characterizations

The Ni/Ni(OH)₂ nanoflakes (Ni/Ni(OH)₂-NFs) catalyst was chemically prepared at room temperature (25 °C) using a new and versatile approach of a soft hexagonal liquid crystal template and sodium borohydride (NaBH₄), as shown above in Scheme 1. The NaBH₄ acted as a bi-functional agent of chemically reduced the dissolved nickel ions intestinal aqueous domain of hexagonal LCT, as well as, the concurrently evolved hydrogen gas exfoliated and scale off the intestinal deposited catalyst layers that ended up as the nanoflake powder. The surface morphology of the as-prepared Ni/Ni(OH)₂ nanoflakes were studied using scanning (SEM) and transmission (TEM) electron microscopy and is shown in Fig. 1. The SEM images



Fig. 1 SEM image of Ni/Ni(OH)₂-NFs (a) and (b) at different magnification, (c) TEM of Ni/Ni(OH)₂-NFs and (d) TEM of bare-Ni (OH)₂.

in Fig. 1a and 1b, with different magnifications, clearly show that the obtained Ni/Ni(OH)2 had a 2D nanoflake-like surface morphology. The Ni/Ni(OH)2 nanoflakes had a random aggregation of numerous and strongly crumpled 2D nanoflakes with a considerably thin thickness and open mesoporous channels. Moreover, the SEM surface morphology image of the bare-Ni (OH)₂ shown in Fig. S1 (Supporting Information) shows the bare-Ni(OH)₂ deposit has very large irregular particles in micrometer size in contrast to the 2D very thin nanoflakes morphology of the Ni/Ni(OH)2-NFs catalyst. The analysis using the energy-dispersive X-ray spectroscopy (EDX) and SEM-mapping in Fig. S2 has revealed no evidence for the presence of nickel boride/borate deposit and the Ni:O mole ratio is very close to 1:2 as shown in the results in Table S1. These analyses indicate that all the boron from the NaBH₄ reducing agent has been completely washed away and no evidence for the formation of nickel boride/borate (Gupta et al., 2020). In addition, the TEM images in Fig. 1c verify that the 2D flake-like morphology was similar to the 2D-graphene appearance and that the flakes were overlapping and have an ultrathin nature with an estimated thickness of 10.0 nm that was consistent with the hexagonal aqueous domain thickness of the Brij®78 surfactant. Note that the size of the nanoflakes could be extended over a few hundreds of nanometres, which made these nanoflakes significantly larger than those deposited from a bulk liquid crystal template, as reported in our previous work (Ghanem et al., 2015; Ghanem et al., 2017). Moreover, the TEM image of the *bare*-Ni(OH)₂ sample prepared in the absence of the Brij®78 surfactant shown in Fig. 1d revealed the formation of a very dense and nonporous deposit morphology.

The crystal structural details of the Ni/Ni(OH)₂-NFs were examined by X-ray diffraction (XRD). As shown in Fig. 2, the diffraction peaks were broad, which indicated the formation of a semi-crystalline structure. The peaks diffraction observed at 12.07, 25.38, 33.68, 36.35, and 59.98 could be indexed to the (001), (002), (110), (111), and (300) diffraction planes, respectively, of the α -Ni(OH)₂ phase (JCPDS card no. 38–0715). While the peaks diffraction at 20 = 44.55 and 70.98 matched well with the (111) and (220) planes for the pure nickel phase structure, which confirmed the formation of the Ni/ α -Ni(OH)₂ mixture of the nanoflakes (Hall et al., 2015). In comparison, the X-ray diffraction pattern of the *bare*-Ni(OH)₂ in Fig. S1 reveals a similar crystal structure to



Fig. 2 (a) X-ray diffraction pattern of the Ni/Ni(OH)₂-NFs, (b) Nitrogen adsorption–desorption isotherms of Ni/Ni(OH)₂-NFs, and (c) pore size distribution calculated using the Barrett–Joyner–Halenda (BJH) method.

the Ni/Ni(OH)₂-NFs catalyst. The adsorption–desorption isotherm curve and the pore size distribution of Ni/Ni(OH)₂-NFs are shown in Fig. 2b and 2c, respectively. The isotherm exhibited type IV (H₃) according to the IUPAC classification of the adsorption–desorption isotherm (Sing, 1985), and the hysteresis loop in the relative pressure range of 0.45–1.0 was related to the capillary condensation of N₂ gas, which revealed the presence of disordered lamella and the slit shape of the mesoporous structure was consistent with the nanoflake structure of Ni/Ni (OH)₂-NFs. From the isotherms, the BET-specific surface area of the Ni/Ni(OH)₂-NFs was estimated at 135 ± 5.0 m²/g. The pore size distribution curve is shown in Fig. 2c obtained by the BJH method further confirmed the size of the confined mesopores is in the range of 6.0–20.0 nm and centered around 10.0 nm for the Ni/Ni(OH)₂-NFs catalyst.

3.2. Electrochemical characterizations of Ni/Ni(OH)₂-NFs

The Ni/Ni(OH)₂-NFs and *bare*-Ni(OH)₂ catalysts were characterized by cyclic voltammetry (CV), chronoamperometry, and impedance measurements in the alkaline solution to investigate the electroactivity and performance toward the oxidation and sensing of glucose molecules. Fig. 3a shows the successive multicyclic voltammograms (CV) of the Ni/Ni $(OH)_2$ -NFs electrode at a potential scan rate of 50 mV s⁻¹ in the 2.0 M KOH solution. During the first cycle, anodic and cathodic redox peaks were observed at the potential of 0.465 and 0.215 V vs. Ag/AgCl, respectively, which could be assigned to the well-known redox couple of Ni(II)/Ni(III) according to the reaction of $(Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-)$ (Desilvestro et al., 1988; Barnard and Randell, 1983; El-Shafei, 1999; Hall et al., 2015). The electrochemical conversion of the Ni/Ni(OH)2-NFs catalyst to nickel oxyhydroxide (NiOOH) can be explained following the mechanism reported by Medway et al. (Medway et al., 2006) suggesting that the Ni/ Ni(OH)₂-NFs catalyst is formed from non-stoichiometric Ni and α -Ni(OH)₂ with buffer (1–2) layers of NiO in-between $(Ni/NiO/\alpha-Ni(OH)_2)$ due to the reaction with air/moisture as shown by X-ray diffraction above. Upon immersion in KOH solution and at open circuit potential, most of the Ni and



Fig. 3 (a) The successive multicyclic voltammograms (CV) of the Ni/Ni(OH)₂-NFs electrode at a potential scan rate of 50 mV s⁻¹ in the 2.0-M KOH solution, (b) cyclic voltammograms at 50 mV s⁻¹ for mesoporous Ni/Ni(OH)₂-NFs with different loading in comparison of 100 μ g of bare-Ni(OH)₂ (black) in 2.0 M KOH solution, (c) plot for anodic and cathodic peak current density versus Ni/Ni(OH)₂-NFs catalyst loading, (d) effect of potential scan rate on cyclic voltammogram of 150 μ g of Ni/Ni(OH)₂-NFs catalyst in 2.0 M KOH solution, (e) plot for the relationship between redox peak current and the square root of the scan rate.

NiO are converted to thicker α -Ni(OH)₂ layer. On positive potential scan above Ni(II)/Ni(III) redox potential, the α -Ni

(OH)₂ is oxidized to β -NiOOH layer, as well as the remaining Ni and NiO, are reacted with OH⁻ ion and converted to β -

NiOOH via the reactions of (NiO + OH⁻ \rightarrow NiOOH + e⁻) and (Ni + $3OH^- \rightarrow NiOOH + e^-$) respectively. In addition, the little anodic peak around 0.5 V vs. Ag/AgCl could be related to the oxidation of β -Ni(OH)₂ to β -NiOOH (Medway et al., 2006). By continuing cycling, the peak current grew with the potential scans and the redox peaks shifted to a more negative potential and then stabilized mid-peak at approximately 0.295 V vs. Ag/AgCl and the peak separation ($\Delta E = E_{anodic} - E_{anodic}$ Ecathodic) decreased. This presumably indicated the progressive enrichment of the accessible Ni(II)/Ni(III) active sites with a change in the Ni/Ni(OH)₂-NFs to β -NiOOH crystal structure and the reaction became more reversible upon prolonged cycling (Luo., et al., 2012, Visscher and Barendrecht, 1983). Moreover, the cyclic voltammograms in Fig. 3a showed that beyond the anodic peak at a more positive potential of > 0.60 V, the current increased as a result of the commencement of the oxygen evolution reaction; this was consistent with the relevant reported results (Danaee et al., 2008). The effect of Ni(OH)₂-NFs loading was investigated by carrying out the CVs at different loadings using carbon paper (CP) electrodes in 2.0 M KOH. Fig. 3b displays the cyclic voltammograms of the Ni/Ni(OH)₂-NFs with different loadings of 20, 50,100, and 150 µg in evaluation with 100 µg of *bare*-Ni(OH)₂ (black line) obtained using a carbon paper substrate in a 2.0 M KOH solution at a scan rate of 50 mV s^{-1} and via 10 cycles of voltammetry. It can be seen that the Ni(OH)2-NFs showed well-defined Ni(II)/Ni(III) characteristic redox peaks located at the midpoint potential of approximately 0.295 V vs. Ag/ AgCl. The characteristic Ni(II)/Ni(III) redox peak current gradually increased when the loading of Ni(OH)2-NFs increased, and the CV of Ni(OH)2-NFs in the alkaline solution was very stable during the performed 10 cycles and the redox peak current was almost the same as that shown in Fig. 3a. Furthermore, the redox peak current was significantly higher than that for the *bare* nickel hydroxide with similar loading, which revealed the unique nanoflake structure with a high percentage of porosity and an enhanced electrochemical active surface area (ECSA), which facilitated the mass transport of the electrolyte OH⁻ to the surface of Ni(OH)₂ and a fast diffusion rate during the redox process (Tong et al., 2012; Wang et al., 2019). The electroactive surface area (ECSA) of Ni (OH)₂-NFs was further calculated according to the equation (ECSA = Q/(mq)), where Q is the reduction peak charge of NiOOH to Ni(OH)₂, *m* is the catalyst loading mass, and *q* is the Ni(OH)₂ monolayer formation charge that equivalent to 257 μ Ccm⁻² (Yan et al., 2014; Wang et al., 2012). The ECSA obtained for the Ni/Ni(OH)2-NFs and bare-Ni(OH)2 electrodes was equal to approximately 361.3 and 24.5 m² g⁻¹, respectively. The ECSA achieved in the case of Ni/Ni(OH)2-NFs was approximately 15 times higher than that of the ECSA of bare-Ni(OH)2, which confirmed that the Ni/Ni(OH)2-NFs catalyst exhibit a considerably higher electroactive surface area than bare-Ni(OH)₂ because of the formation of ultrathin nanoflakes. Moreover, Fig. 3c shows the oxidation and reduction peak currents linearly increased as the catalyst loading increases with the anodic and cathodic slope are 0.352 and -0.287 mA/µg, respectively. This current enhancement was attributed to increasing the active site density and indicated that the Ni(OH)2-NFs had an open porous framework that facilitated the mass diffusion of the electroactive species irrespective of the film thickness. To examine the nature of the Ni(OH)₂-NF redox process at the electrode surface, the CV

was executed at different scan rates ranging from 5 mV s⁻¹ to 50 mV s⁻¹, as shown in Fig. 3d. We found that as the scan rate increased, the anodic peak shifted slightly to the positive potential, whereas the cathodic peak moved negatively. In addition, the redox peak currents increased linearly with the square root of the scan rate, as illustrated in Fig. 3e, which indicated that the reaction of the hydroxide ions and the formation of β -NiOOH was a diffusion-controlled process, which was consistent with the reported results (Sing, 1985; Lu et al., 2015a).

3.3. Non-enzymatic oxidation of glucose at Ni/Ni(OH)₂-NFs electrode

The non-enzymatic oxidation of glucose using Ni/Ni(OH)2-NFs was performed in an alkaline solution of 2.0 M KOH; Fig. 4a illustrates the cyclic voltammograms (CVs) at 50 mV s⁻¹ of the Ni(OH)₂-NFs (150 µg loading) at a different concentration range of 5.0 to 40.0 mM of glucose. As can be seen in Fig. 4a, upon the addition of glucose, the CVs followed the profile of the Ni/Ni(OH)2-NFs redox system with the oxidation peak current gradually increasing upon the addition of more glucose, which indicated the significant catalytic activity of Ni(OH)2-NFs toward glucose oxidation in the alkaline solution. Moreover, the onset and peak potential of anodic Ni(II) oxidation slightly shifted to a more positive value as the glucose concentration increased, apparently indicating the good interaction/adsorption of the glucose molecules with the Ni (II) active sites. As shown in Fig. 4b, the plot of the anodic peak current linearly increased with the bulk glucose concentration, and the line slope was equal to $1.253 \text{ mA/cm}^2 \text{ mM}$. In contrast, the cathodic peak current gradually decreased upon the addition of more glucose and the ratio of the anodic/cathodic peak currents in the absence and presence of 40 mM glucose significantly increased from 1.45 to 10.85, indicating the indirect glucose oxidation at the Ni/Ni(OH)2-NFs surface that followed the well-documented electrochemical-chemical (EC) reaction mechanism (Zhang et al., 2011; Gao et al., 2016). In addition, during the reverse scan, the glucose oxidation continued at the positive potential and the current showed a maximum because of the regeneration of more Ni(III) active sites followed by the current drop as the cathodic potential approached. Basically, and according to Flishmann et al. (Fleischmann et al., 1971; Fleischmann et al, 1972), the EC mechanism of glucose oxidation at the nickel-based catalysts occurs through the Ni^{2+}/Ni^{3+} redox couple according to the electrochemical reactions in the following equations.

 $Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$ (1)

$$NiOOH + glucose \rightarrow Ni(OH)_2 + glucolactone$$
 (2)

Here, at the applied anodic potential, the Ni²⁺ ions were oxidized to Ni³⁺, as shown in Eq. (1). Then, glucose chemically oxidized to glucolactone at the electrogenerated Ni³⁺ active sites according to Eq. (2); thereafter, the cathodic peak around 0.220 V vs. Ag/AgCl became weaker upon the addition of more glucose, which suggested that more NiOOH active sites were used for the indirect glucose oxidation reaction. Accordingly, the Ni/Ni(OH)₂ nanoflakes catalyst exhibit enhanced electroactive surface area of Ni(II)/Ni(III) active sites where the glucose molecules can be adsorbed and oxidized



Fig. 4 (a) Cyclic voltammograms at 50 mV s⁻¹ for 150 µg mesoporous Ni/Ni(OH)₂-NFs catalyst in 2.0 MKOH in presence of different concentration (0, 5, 10, 20, 30, 40) mM of glucose, (b) plot of the anodic and cathodic peak current against the glucose oxidation, (c) cyclic voltammograms at 50 mV s⁻¹ for different loading of Ni/Ni(OH)₂-NFs catalyst in 20 mM glucose and 2.0 MKOH, and (d) plot of glucose oxidation peak current against catalyst loading.

to glucolactone *via* the EC mechanism. Moreover, the linear detection range of glucose oxidation has been increased up to 60 mM using Ni(OH)₂-NFs catalyst (Figs. 4b and 7b below) which indicates enhanced accessibility and tolerance to the adsorption of glucose oxidation intermediates and products at Ni(II)/Ni(III) active sites due to high surface area of an open mesoporous 2D nanoflakes architecture.

The Ni/Ni(OH)₂-NFs catalyst loading had a significant influence on the glucose oxidation catalytic current, as shown in Fig. 4c and 4d. The CVs of the Ni/Ni(OH)₂-NFs catalyst

with different loadings (Fig. 4c) in comparison to bare-Ni $(OH)_2$ were recorded at 50 mV s⁻¹ in 20 mM glucose dissolved in 2.0 M KOH. The *bare*-Ni(OH)₂ exhibits a small catalytic effect for glucose oxidation (Fig. 4c, black line). Moreover, the oxidation peak current of 20 mM glucose at 200 µg Ni/ Ni(OH)₂/NFs electrode was about 67 mA, which was much larger (up to 13 times) than that at *bare*-Ni(OH). Furthermore, the glucose oxidation peak potential was shifted by 50 mV less positive (0.46 to 0.41 V) at Ni/Ni(OH)-NFs than *bare*-Ni(OH)₂ which signifies the superior electrocatalytic activity towards glucose oxidation at Ni/Ni(OH)-NFs. Fig. 4d depicts the correlation between the glucose oxidation peak current and the catalyst loading exhibited a volcanic plot profile, where the glucose maximum oxidation peak current (67.3 mA/cm²) was achieved at around 200 μ g of the catalyst loading. The glucose oxidation peak current linearly increased during the ascending



Fig. 5 (a) CVs for 150 μ g Ni/Ni(OH)₂-NFs catalyst in 2.0 MKOH at different with 20 mM glucose at different scan rates, and (b) plot for the relationship between redox peak current and the square root of the scan rate.



Fig. 6 EIS Nyquist diagram and equivalent circuit of Ni/Ni(OH)₂-NFs and bare-Ni(OH)₂ electrodes in 10 mM glucose and 2.0 M KOH solution.

Table 1The equivalent circuit parameters values of the EISspectra of glucose oxidation at the Ni/Ni(OH)2-NFs and bare-
Ni(OH)2 electrodes.

Element	Ni/Ni(OH)2-NFs	bare-Ni(OH) ₂	
$R_{s}(\Omega)$	1.2249	1.3004	
C ₁ , mF	2.175	0.330	
R_1, Ω	0.14704	0.31819	
Q ₁ , mF	41.44	8.95	
R ₂ , Ω	3.58	11.073	

part of the volcanic behavior, which could be attributed to the increase in the electrochemical active surface area of the Ni/Ni $(OH)_2$ -NFs catalyst as the catalyst loading increased (as shown above in Fig. 3b). In contrast, the decrease in the glucose oxidation current above a catalyst loading of above 200 µg could be related to the electron transfer retardation and the limitation of OH⁻ diffusion within a thicker catalyst film (El-Shafei, 1999; Pournaghi-Azar and Habibi, 2007). The electro-oxidation of glucose on a Ni(OH)₂-NFs electrode was investigated in 20 mM glucose and 2.0 M KOH solution at different scan rates in the range of 5–100 mV/s. The redox peak current increased gradually with an increase in the scan rate in the presence of glucose, as shown in Fig. 5b. The linear



Fig. 7 (a) Chronoamperometric response of the Ni/Ni(OH)₂-NFs electrode at various applied potentials in 2.0 M KOH with the successive addition of (1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 40, 50 and 60) mM glucose, (b) The corresponding calibration plots of oxidation current density and glucose concentration at various applied potentials in 2.0 M KOH, (c) Chronoamperometric response of the Ni/Ni (OH)₂-NFs electrode in different concentrations of KOH with the successive addition of (1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 40) mM glucose, and (d) plots for the calibration curves for oxidation current and glucose concentration in different concentrations of KOH solution at an applied potential of 0.6 V *vs.* Ag/AgCl.

relationship between the redox peaks currents and square root of the scan rate was validated by the regression equations: $I_{pa}(-mA/cm^2) = 5.35X + 11.565 (R^2 = 0.9982)$ and $I_{pc} (mA/cm^2) = -2.498X + 5.234 (R^2 = 0.9969)$, respectively (Fig. 5b). This result indicated that the reaction of glucose on the Ni(OH)₂-NF surface was under a mass diffusion-controlled process (Li et al., 2013; Qiao et al., 2020).

The electron transfer capability of the Ni/Ni(OH)₂-NFs electrode was investigated by electrochemical impedance spec-

troscopy (EIS). Fig. 6 display the Nyquist plots of the Ni/Ni (OH)₂-NFss and *bare*-Ni(OH)₂ electrodes in 2.0 M KOH containing 10 mM glucose at an applied potential of 0.65 V *vs*. Ag/ AgCl and frequency range from 0.01 to 10^5 Hz. In the highfrequency region, the Nyquist diagrams show a depressed very small semicircle while in the low-frequency region a second increasingly big semicircle can be observed. As shown in Fig. 6 (inset) the depress semicircle in the high-frequency region can be likely related to the catalyst interaction with



Fig. 8 (a) Chronoamperometric responses of the Ni/Ni(OH)₂/NFs and bare-Ni(OH)₂ electrodes with successive addition of different glucose concentrations range from 0.2 to 13 mM in 2.0 M KOH at 0.60 V vs. Ag/AgCl, and (b) the corresponding calibration plot of glucose oxidation current density against the glucose concentration.

carbon paper (CP) substrate. On the other hand, the large semicircle in the low-frequency region with the characteristic frequency of 1.745 and 3.175 Hz for Ni/Ni(OH)2-NFs and bare-Ni(OH)₂ respectively could be related to the impedance of glucose oxidation at electroactive Ni(OH)₂/NiOOH redox system. As shown above (Eqs. (1) and (2)) the NiOOH species chemically catalyzes the oxidation of glucose, while itself is reduced back to Ni(OH)₂. Therefore, there is a continuous electrochemical re-oxidation of Ni(OH)2 to NiOOH as well as chemical oxidation of glucose (Zheng et al., 2018). The Nyquist diagram of the glucose oxidation at the Ni/Ni (OH)₂-NFs and *bare*-Ni(OH)₂ electrodes can be fitted to the equivalent circuit illustrated in the inset in Fig. 6. However, the equivalent circuit capacitor (Q_1) in the low-frequency region is replaced by a constant phase element (CPE)Q due to the electrode nanoarchitecture and roughness which cause inhomogeneous distribution in double-layer capacitance and solution resistance (Danaee et al., 2008). The parameters of the equivalent circuit are defined as R_s is the solution resistance, R_1 , the charge transfer resistance, C_1 , double-layer capacitance at the catalyst/carbon paper interface while R2 is the charge transfer resistance and Q_1 is the equivalent CPE capacitance of the glucose oxidation at Ni(OH)2/NiOOH interface. Table 1 reports the values of the equivalent circuit parameters of the EIS spectra of glucose oxidation at the Ni/ Ni(OH)₂-NFs and bare-Ni(OH)₂ electrodes. At the catalyst/carbon paper interface, the Ni/Ni(OH)2-NFss electrode shows lower charge transfer resistance R_1 (0.147 Ω) and about sixtime higher double-layer capacitance C_1 (2.175 mF) than that of the bare-Ni(OH)₂ ($R_1 = 0.318 \Omega$, $C_1 = 0.330 mF$) electrode. A similar impedance trend was obtained for the glucose oxidation at Ni(OH)2/NiOOH interface where the Ni/Ni (OH)₂-NFs exhibit much lower R_2 (3.58 Ω) and higher Q_1 (41.44 mF) values than the bare-Ni(OH)₂ electrode. The EIS analysis signifying the effectiveness of Ni/Ni(OH)2-NFs for lower charge transfer resistance and higher Ni(OH)₂/NiOOH active sites available for glucose adsorption and oxidation.

For the non-enzymatic glucose detection using the Ni/Ni $(OH)_2$ -NFs electrode and to optimize the potential required for the direct glucose sensing at the Ni/Ni $(OH)_2$ -NFs electrode, the results in Fig. 7a show the chronoamperometry at different oxidation potentials of 0.45, 0.50, 0.55, and 0.60 V *vs*. Ag/AgCl in the presence of different glucose oxidation rates

in the 2.0 M KOH solution. The data shown in Fig. 7a reveal that the glucose oxidation current at the Ni/Ni(OH)2-NFs electrode increased with the stepwise addition of different glucose doses (1-60 mM) into 2.0 M KOH, at the studied applied potential. Fig. 7b shows the plot for the correlation between the glucose oxidation current and the concentration at the above-mentioned potential range. Interestingly, at an applied potential of 0.60 V vs. Ag/AgCl, the glucose oxidation current exhibited a good linear relationship with an increase in the glucose concentration of up to 60 mM, which indicated that the Ni/Ni(OH)₂-NFs electrode had a better tolerance for the adsorption of glucose oxidation products and the intermediate. The linear correlation followed the regression equation of I $(mA/cm^2) = 1.078 X + 0.280 (mM)$ and correlation coefficient $(\mathbf{R}^2) = 0.998$. In contrast, at an applied potential of less than 0.6 V, the glucose oxidation current increased linearly up to around 30 mM glucose, and then, the line slope started to decrease. Therefore, all the amperometry measurements were carried out at 0.60 V vs. Ag/AgCl and by the successive addition of glucose into 2.0 M KOH under continuous stirring with a magnetic stirrer. The effect of different concentrations of KOH on the glucose-sensing performance of the Ni/Ni (OH)₂-NFs electrode was investigated and is illustrated in Fig. 7c and d. The results revealed that upon the successive addition of glucose, the oxidation current of the Ni/Ni (OH)₂-NFs electrode response linearly increased and the line slope slightly increased in the order of 0.5 M > 1.0 M > 2. 0 M KOH solution. However, a linear current response deviation was observed in the 0.5-M KOH solution and at a glucose concentration above 35 mM, where the oxidation current started to saturate. This could be attributed to the reaction competition between the Ni(II)/Ni(III) oxidation and the adsorption of glucose molecules at a lower concentration of the KOH solution (Maritan and Toigo, 1990). Therefore, a 2.0 M KOH solution was preferred as the electrolyte for all the chronoamperometry experiments because the response current in 2.0-M KOH was higher than at other concentrations.

Fig. 8a shows the chronoamperometry curves of the Ni/Ni $(OH)_2$ -NFs catalyst with different doses of glucose within the range of 0.2–13 mM in 2.0 M KOH in comparison to the *bare*-Ni(OH)₂ and at an applied potential of 0.60 V *vs.* Ag/AgCl under continuous stirring. The electrode showed a significant response even at a glucose concentration of as low as

Table 2The Ni/Ni(OH)₂-NFs catalyst glucose sensing performance in comparison with some nickel-based glucose sensors reported inthe literature.

Electrode	Sensitivity (mA mM ⁻¹ cm ⁻²)	Linear range	Detection Limit (LOD)	Reference
Ni(OH) ₂ -graphene/GCE Ni(OH) ₂ -HS/GCE	0.494	10–1000 μM 0 8749 μM-7 781 mM	0.6 μM 0.1 μM	(Qiao and Zheng, 2012) (Lu et al. 2015a)
Roselike- Ni(OH)2/GCE	0.419	$0.87 \ \mu M - 10.53 \ m M$	0.08 μM	(Lu et al., 2015a) (Lu et al., 2015b)
Macro-mesoporous Ni(OH) ₂ /GCE	0.243	0.01–8.3 mM	1.0 μM	(Fan et al., 2014)
Ni(OH) ₂ /TiO ₂	0.192	0.03–14 mM	8.0 μM	(Gao et al., 2016)
Ni(OH) ₂ -MOF	1.192	0.5–8.0 mM	0.125 μM	(Zheng et al., 2018)
Ni(OH) ₂ HPA/GCE	1.843		0.23 μM	(Tian et al., 2018)
Ni(OH) ₂ /3DGF/NF	2.366	2–200 µM	0.32 μM	(Mao et al., 2019)
Ni/Ni(OH) ₂ -NFs/CP	1.078	0.2–60 mM	0.8 mM	This work

0.2 mM and fast response (within 4–5 s) toward the stepwise addition of glucose with various concentrations. In contrast and as shown in Fig. 8a, the *bare*-Ni(OH)₂ shows a slight response compared with the response of Ni/Ni(OH)₂-NFs for each addition of glucose, which is consistent with results observed in cyclic voltammetry shown in Fig. 4c. Fig. 8b results provides that the Ni/Ni(OH)₂-NFs sensor displayed a good linear relationship in the range of 0.2 to 13.0 mM of glucose with the regression equation of I(mA/cm²) = 1.0781X + 0.322 (mM) and correlation coefficient (R²) = 0.9979. The achieved limit of detection (LOD) of glucose at the Ni/Ni (OH)₂-NFs electrode reached 0.2 ± 0.02 mM (S/N = 3), while the sensitivity of the present non-enzymatic glucose sensor

reached 1.078 mA/cm² mM⁻¹ which is about four times much higher than that of the *bare*-Ni(OH)₂ electrode (0.225 mA/cm² mM⁻¹) as shown in Fig. 8b. The sensor performance in comparison to our Ni/Ni(OH)₂-NFs sensor with that recently reported non-enzymatic glucose nickel-based sensors is reported in Table 2. Our Ni/Ni(OH)₂-NFs electrode exhibited significantly higher sensitivity (1.078 mA cm⁻² mM⁻¹) and a wider current/[glucose] linear range (0.2–60 mM) than most non-enzymatic nickel-based sensors such as the Ni(OH)₂-graphene/GCE (0.494 mA cm⁻² mM⁻¹) (Qiao and Zheng, 2012) and macro-mesoporous Ni(OH)₂/GCE (0.243 mA cm⁻² mM⁻¹) recently reported (Fan et al., 2014). Although the Ni (OH)₂ HPA/GCE (1.843 mA cm⁻² mM⁻¹) (Tian et al., 2018)



Fig. 9 (a) chronoamperometric response of Ni/Ni(OH)₂-NFs electrode toward the addition of AA, UA, and NaCl interferent species to 1.0 mM glucose in 2.0 M KOH solution and (b) long-term chronoamperometric response of Ni/Ni(OH)₂-NFs electrode in 2.0 KOH in presence of 1.0 and 40.0 mM glucose at 0.6 V vs. Ag/AgCl and (c) the histogram for the maintained glucose oxidation current percentage for 30 days of the Ni/Ni(OH)₂-NFs catalyst stored at ambient room condition.

and Ni(OH)₂/3DGF/NF (2.366 mA cm⁻² mM⁻¹) (Mao et al., 2019) catalysts showed higher glucose sensitivity, our Ni/Ni (OH)₂-NFs showed a significantly wider linear current/[glucose] range of up to 60 mM concentration, which made the Ni/Ni(OH)₂-NFs catalyst more applicable to the sensing of a higher level of glucose concentration. In addition, the Ni/Ni (OH)₂-NFs catalyst was easy to fabricate using a one-pot template synthesis approach at ambient conditions. The Ni/Ni (OH)₂-NFs catalyst sensing performance toward glucose oxidation could be attributed to the higher surface area, 2D hierarchically mesoporous nanoflake architecture, and the excellent electrical conductivity and tolerance for the adsorption of glucose oxidation products and intermediates.

3.4. Selectivity and stability of Ni/Ni(OH)₂/NFs sensor

The influence of the common interfering species such as uric acid (UA), ascorbic acid (AA), and NaCl was analyzed to investigate the selectivity of the Ni/Ni(OH)2-NFs toward glucose oxidation. Fig. 9a displays the chronoamperometric signals of 2.0 M KOH solution containing 1.0 mM glucose at the Ni/Ni(OH)2-NFs electrode surface in the presence of the successive addition of 10 mM UA, AA, and NaCl interferences. We observed that the chronoamperometry exhibited no significant signal increase for the UA and NaCl interferences. However, a significant oxidation current increase was observed when 10 mM AA was added which indicates an electrochemical interference during the glucose oxidation at the Ni/Ni(OH)₂-NFs electrode. The AA interference is commonly observed in glucose amperometric biosensors and can be minimized by modifying the electrode by a selective membrane (Yuan et al., 2005). In addition, the significant activity of the Ni(OH)2-NFs towards ascorbic acid oxidation can be beneficial to develop an amperometric sensing platform for AA and these studies are currently in progress. This result indicated the selectivity of the electrode to both glucose and ascorbic acid. For the stability and efficiency study of the Ni/Ni (OH)₂-NFs electrode for the electrochemical glucose oxidation, Fig. 9b shows the chronoamperometry signal response during a long oxidation period and after the successive addition of 1.0 mM and 40 mM glucose into the stirred 2.0 M KOH at 0.6 V vs. Ag/AgCl. The data showed that the current density signal was extremely stable for more than one hour with no change observed in the presence of either the low (1.0 mM) or the high (40.0 mM) concentration regime of glucose. Moreover, Fig. 9c shows the long-term durability of the Ni/Ni(OH)₂-NFs catalyst during storage in air for 30 days. The catalyst was tested every 5 days by conducting the cyclic voltammetry at a scan rate of 50 mV s⁻¹ in 20 mM glucose dissolved in 2.0 M KOH solution using 150 µg loading of Ni/Ni (OH)₂-NFs catalyst. The histogram in Fig. 9c clearly shows the catalyst maintained more than 95% of the glucose oxidation current after 30 days demonstrating the long-term durability of the Ni/Ni(OH)2-NFs catalyst.

4. Conclusions

The nanoflakes of a nickel/nickel hydroxide (Ni/Ni(OH)₂) catalyst were synthesized at room temperature via a double template of liquid crystal and in-situ hydrogen effervesce approach. The dissolved nickel ions in the interstitial aqueous domain of the Brij®78 surfactant

hexagonal phase were chemically reduced by sodium borohydride that simultaneously generated excessive hydrogen bubbles and exfoliated the nickel layers. The Ni/Ni(OH)2-NFs physicochemical characterizations proved the formation of the semi-crystalline Ni/Ni(OH)2 nanoflake morphology having a specific surface area of 135 m^2/g and a thickness of approximately 10 nm. The Ni/Ni(OH)2 nanoflakes exhibited superior glucose non-enzymatic sensing activity and stability to that of the bare-Ni(OH)₂ prepared without the Brij®78 surfactant. The Ni/Ni(OH)₂ nanoflakes showed that the glucose-sensing linear dependence range extended over from 0.2 to 60 mM with a sensitivity of 1.078 mA/cm² mM and a detection limit of 0.2 \pm 0.02 mM (S/ N = 3). Moreover, the EIS analysis revealed that the kinetics and the charge transfer resistance of the glucose oxidation were significantly enhanced at the Ni/Ni(OH)2 nanoflakes. In addition, minimum signal interference was observed upon the addition of 10 mM uric acid and NaCl interferences during the analysis of glucose, while a substantial current enhancement was obtained when 10 mM AA was added. The enhancement of the non-enzymatic glucose sensing of Ni/Ni (OH)2-NFs could be related to the 2D nanoflake mesoporous nanoarchitecture with a highly porous channel and conductivity, which facilitated the access of the electroactive species to the nanoflake surface. The results revealed that our Ni/Ni(OH)2-NFs catalyst had excellent electrocatalytic glucose oxidation activity and durability and could be a good candidate catalyst for the glucose non-enzymatic sensing in an alkaline solution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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