

Carbon-coated nickel foam for hypochlorous acid sensor

Afiten R. Sanjaya ^{1*}, Hanzhola G. Riyanto ¹, Isnaini Rahmawati ¹, Yulia M. T. A. Putri ¹, Dede Nurhalimah ¹, Endang Saepudin ¹, Yudhistira Tesla ², and Yuni K. Krisnandi ¹

1 Department of Chemistry, Mathematics and Natural Sciences, Universitas Indonesia; Campus UI Depok, Depok 16424, Indonesia

2 Singota Solutions, Bloomington, Indiana, 47401, USA

* Correspondence: afiten.rahmin@sci.ui.ac.id

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Abstract

The electrochemical detection method of hypochlorous acid (HOCl) using carbon foam electrodes have been successfully developed. The carbon foam was prepared from carbon-coated nickel foam which is synthesized using a hydrothermal-carbonization method. SEM characterization indicated that the optimum synthesis of carbon-coated nickel foam has been achieved on the 4th layer coating process with an expected spherical structure, while characterization using FTIR and Raman spectroscopy confirmed the formation of graphitic material with D band and G band characteristics. An electroactive surface area of 0.0236 cm² was achieved. Cyclic voltammetry of HOCl in 0.1 M phosphate buffer solution pH 6.0 showed the best current response for HOCl reduction occurs at a potential of -0.3 V (vs. Ag/AgCl). Further detection of HOCl using amperometry technique in the concentration range of 2-200 µg/mL showed good linearity with sensitivity of 9.112 mA/µg/L and an estimated detection limit of 1.96 µg/mL. Good repetition is indicated by the RSD value of 2.499 % (n=5). This developed sensor also showed good selectivity in the presence of interference compounds, such as FeCl₂ and CuSO₄. Besides, the determination of HOCl in tap water has been successfully conducted and generated a comparable result with the UV-VIS method (3.30 µg/mL hypochlorite). The results indicated that the developed sensor is promising for the detection of HOCl in environmental applications.

Keywords: carbon sphere-coated nickel foam; electrochemical sensor; HOCl; hydrothermal-carbonization method; non-enzymatic sensor

1. Introduction

Hypochlorous acid (HOCl) is a type of reactive oxygen species (ROS), which plays an important role in resisting pathogen invasion and maintaining cell redox balance and other physiological processes (Lau et al., 2008; Ulfig & Leichert, 2021; Zuo et al., 2015). HOCl is also widely used as a disinfectant. However, excessive amounts can cause harm to the environment and human health (Duan et al., 2021). As a crucial component of the human immune system, the normal concentration of HOCl in the body typically ranges around 200 µM (Hu et al., 2021). HOCl can also pose health risks if its levels exceed the normal range, as it has high oxidation ability that can lead to diseases such as cardiovascular disease, rheumatoid arthritis, atherosclerosis, and cancer (Andrés et al., 2022; Lau et al., 2008; Martemucci et al., 2022; Zuo et al., 2015). Studies have shown that the use of chlorine-containing disinfectants can increase mortality in zebrafish embryos and the risk of bladder cancer in humans (Duan et al., 2021; Hanigan et al., 2017; Rahmawati et al., 2022). Therefore, developing a fast and efficient method to measure HOCl in environmental and biological samples is critical for ensuring public health and safety.

Various detection methods have been developed including colorimetric (Wonjung et al., 2021), fluorescent (Hu et al., 2021), chemiluminescence (Zhang et al., 2018), and electrochemical methods (Murata et al., 2008). Electrochemical techniques offer a favorable

alternative approach as they require minimum amount of reagents, user-friendly, and possess the ability to provide high sensitivity and long-term response stability (Murata et al., 2008; Zhang et al., 2018). Additionally, these methods offer fast detection measurement, portability, and continuous monitoring with little or no requirement for sample preparation (Rahmawati et al., 2022; Seymour et al., 2020).

Nickel foam (NF) is a versatile material that has recently gained significant attention as an electrode material in electrochemical sensors (Ratsoma et al., 2023). NF possesses a unique three-dimensional interconnected structure and a much larger electrochemically active surface area than traditional electrode materials (Chaudhari et al., 2017; Ratsoma et al., 2023). These properties make it a promising material to be used in electrochemical sensors due to its ability to provide more active electrochemical sites for reactions to occur, enhance material conductivity, and improve the overall electrochemical performance of the sensor with higher sensitivity, selectivity, and stability (Ratsoma et al., 2023).

However, NF electrodes may not exhibit good stability in hypochlorous solutions due to the oxidizing nature of hypochlorite ions, which can cause the oxidation of nickel. This process can result in the formation of nickel oxide or other nickel-based compounds on the electrode surface (Xu & Gao, 2020), ultimately leading to a decrease in its electrochemical performance and stability. Nonetheless, researchers have explored various methods to improve the stability of nickel foam electrodes in hypochlorite solutions. One such method involves modifying the surface of the electrode to protect it from oxidation (Zhang et al., 2022).

Carbon materials possess inherent chemical inertness (dos Santos et al., 2017; Lam & Luong, 2014), which enables them to withstand the oxidative nature of hypochlorous acid. The stable carbon electrode surfaces resist oxidation and maintain their electrochemical properties, even when exposed to hypochlorous solutions. This resilience allows carbon electrodes to retain their structural integrity and electrochemical activity, providing a stable platform for efficient electron transfer and electrochemical reactions (dos Santos et al., 2017; Noor et al., 2021). In this work, the advantage NF with carbon is combined by incorporating carbon on the surface of NF to develop an electrochemical detection system for hypochlorous acid. As expected, good sensitivity of the responses could be achieved with good stability of the response. The results indicated that the carbon-coated NF is promising as an electrode for hypochlorous acid sensors.

2. Methods

2.1. Materials and Instruments

The materials used in this study were isopropanol, sodium hypochlorite (NaClO, 14% purity), potassium iodate (KIO₃), sodium thiosulfate (Na₂S₂O₃·5H₂O), potassium iodide (KI), sodium bicarbonate (NaHCO₃), di-potassium hydrogen phosphate anhydrous (K₂HPO₄), anhydrous potassium dihydrogen phosphate (KH₂PO₄), hydrochloric acid (HCl, 37% purity), starch from potato, ascorbic acid, glucose in analytical grade were purchased from Sigma Aldrich, while the double-distilled water was produced using Millipore Direct-Q® 5 UV. The instrumentation used were potentiostat eDAQ (ER466, Australia), SEM-EDX (TEM, JEOL 5400), FTIR (Shimadzu IR Prestige 21), XRD (Rigaku, Rint-2000), Raman spectroscopy (Renishaw System 2000), and UV-Vis Spectrometer (Thermo Fisher Scientific 1510).

2.2. Preparation Carbon-coated Nickel Foam (C@NF)

Prior to use, the nickel foam was pre-treated by washing using ethanol solution and deionized water and dried at 60°C for 3 hours. Carbon-coated nickel foam was prepared by immersing the pre-treated nickel foam in 0.125 M glucose solution and heated hydrothermally in a Teflon-lined stainless-steel autoclave at 80°C for 24 h. The nickel foam was washed several times using ethanol and water, then dried in the oven at 60°C for 3h. Afterward, the nickel foam was carbonized in a furnace at 550°C for 4 h with heat rate 5°C/min. This treatment was repeated for 1, 2 and 4 times, to determine the effect of cycles towards the surface enhancement of nickel foam electrode.

2.3. Electrochemical study of C@NF for HOCl detection

Electrochemical study of C@NF was carried out using an electrochemical cell with three electrodes. The prepared C@NF was used as the working electrode, while a spiral Pt wire and an Ag/AgCl system were used as the counter and reference electrodes, respectively. Cyclic voltammetry technique in the potential range used was -1 V to +1 V and the scan rate of 100 mV/s was employed with 0.1 M phosphate buffer solution (PBS) as the electrolytes.

2.4. Performance and stability test of C@NF for HOCl detection

The determination of the linear calibration curve was carried out by measuring the current responses of various HOCl concentrations from 2 to 200 µg/L in 0.1 M PBS pH 6.0 using amperometry methods at working potential of -0.3 V for 180 seconds. The repeatability test was carried out by measuring the 50 µg/L HOCl solution at the C@NF electrode for 10 times. Electrode selectivity test was performed by measuring the current response of 50 µg/L HOCl in the presence of 5 mM FeCl₂ and 0.2 mM CuSO₄ as interference species with volume ratio (1:1) v/v.

2.5. Application prepared electrode for HOCl detection in tap water samples

The tap water sample was added with 3 µg/L HOCl solution and then diluted in a 10 mL volumetric flask with 0.1 M PBS pH 6.0. The measurement was conducted at -0.3 V working potential using C@NF electrode, then validated the measurement using a UV-Vis spectrophotometry method.

3. Results and Discussion

3.1. Synthesize C@NF

The modification of nickel foam surface with carbon film was conducted in an oven using hydrothermal method at 180°C for 24 hours. Then, to form the carbon layer, the substrate was carbonized using thermal annealing at 550°C with heating rate 5 °C/minute. FTIR spectra in Figure 1.a show that the synthesized material exposed several specific functional group peaks at round 687, 1030, 1570, 2929, and 3750 cm⁻¹ which are respectively attributed to the C-H bending, C-O stretching, C=C stretching, C-H alkyl stretching and OH stretching. This data is confirmed to the glucose material as the carbon source to form a carbon layer on the surface of NF substrate (Morais et al., 2019). Additionally, the presence of a peak at 458 cm⁻¹ was observed and attributed to the Ni-O stretching of NF materials as the modified substrate (Zhai et al., 2011). Transmittance intensity of the carbon increased linearly with an addition of the carbonized cycle from 1st cycle (C@NF1) until 4th cycle (C@NF4) indicating the mass loading carbon on the 4th cycle is higher than the first cycle.

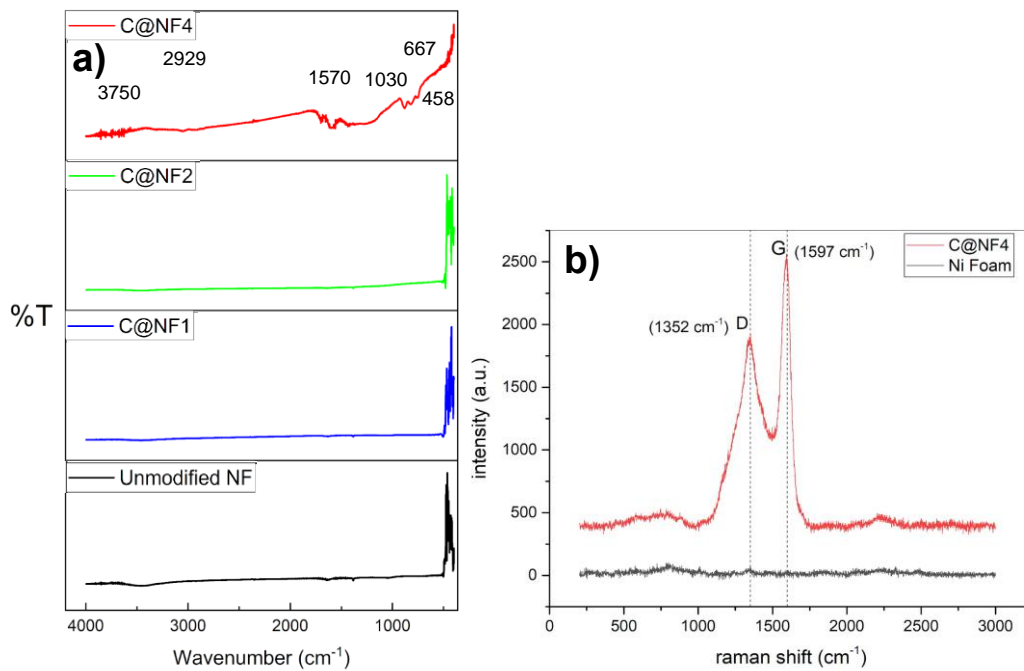


Figure 1. Characterization of the prepared C@NF using a) FTIR and b) Raman spectroscopy

The analysis was also characterized using Raman Spectroscopy to validate the presence of carbon layer on the surface of substrate electrodes, in which D and G band characteristics were observed at 1352 cm^{-1} and 1597 cm^{-1} , respectively (Fig. 1.b). The presence of both Raman shift is contributed to the crystal defect and the presence of sp^2 bond on the carbon layer (Nunes et al., 2022; Rahmawati et al., 2023). Further calculation of the intensity of D and G band ratio showing a specific I_D/I_G ratio 0.74 which is confirmed to the graphite oxide materials (Gao et al., 2022). Both characterizations indicate that modification of carbon material on the nickel foam substrate was successfully performed using hydrothermal and thermal annealing processes with optimum condition at 4th cycle carbonized process.

The surface morphology during the carbonization process was evaluated using SEM-EDS. Figure 2 reveals that increasing the carbonized cycle can enhance the carbon layer on the substrate surface. Increasing the cycle of carbonized process caused the formation of spherical structure of the carbon layer (Figure 2.b and 2.c), while fully covered the nickel foam surface could be achieved at the 4th cycle of the carbonized process (Figure 2.d). The element compositions of the surface were characterized using EDS (Table 1) shows that the nickel foam with 4 times carbonized cycles process contained more carbon elements with 90.13% atom compared to the material from 1 cycle carbonized with 64.40%.

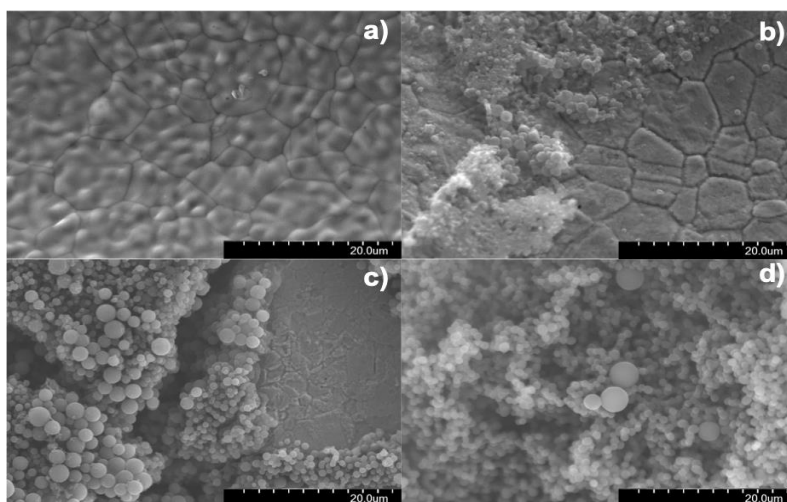


Figure 2. Surface enhancement of carbon sphere-modified nickel foam during the carbonized process from a) the unmodified nickel foam to b), c), d), the first, second and fourth cycles of carbonization, respectively

Table 1. Comparison of the elements on the unmodified and the modified nickel foam

Electrode	Atom (%)		
	C	O	Ni
Nickel Foam	8.42	1.67	89.91
C@NF1	64.40	4.71	30.89
C@NF2	84.97	10.49	4.22
C@NF4	90.13	4.27	5.60
C@NF4-Oxidizing	76.77	12.34	10.89

The SEM EDS was completed by the mapping elements (Figure 3). Comparison between the unmodified nickel foam and C@NF4 clearly shows the presence of carbon material (red color) of the C@NF4 spreading on the surface of the nickel foam. Nevertheless, these morphologies give more electroactive sites that will functionalize on the application of electrodes as a sensor substrate (Zhai et al., 2018). This morphology gives an opportunity to increase the electrochemical performance especially on the highest conductivity and good stability on the reaction which comes from the carbon material (Sanetuntikul et al., 2014; Zhang et al., 2022). It can be seen in Figure 3.c where the electrode still retains stable morphology with carbon layer which confirmed using EDS mapping of C@NF4. Therefore, after the application process the active site of the prepared decreased in consequence of the leaching process of carbon layer from the nickel foam substrate when the redox reaction held on the surface of electrode in the hypochlorite detection. This phenomenon was observed on the decreasing of carbon element from 90.13% to be 76.77% at the end of the application process.

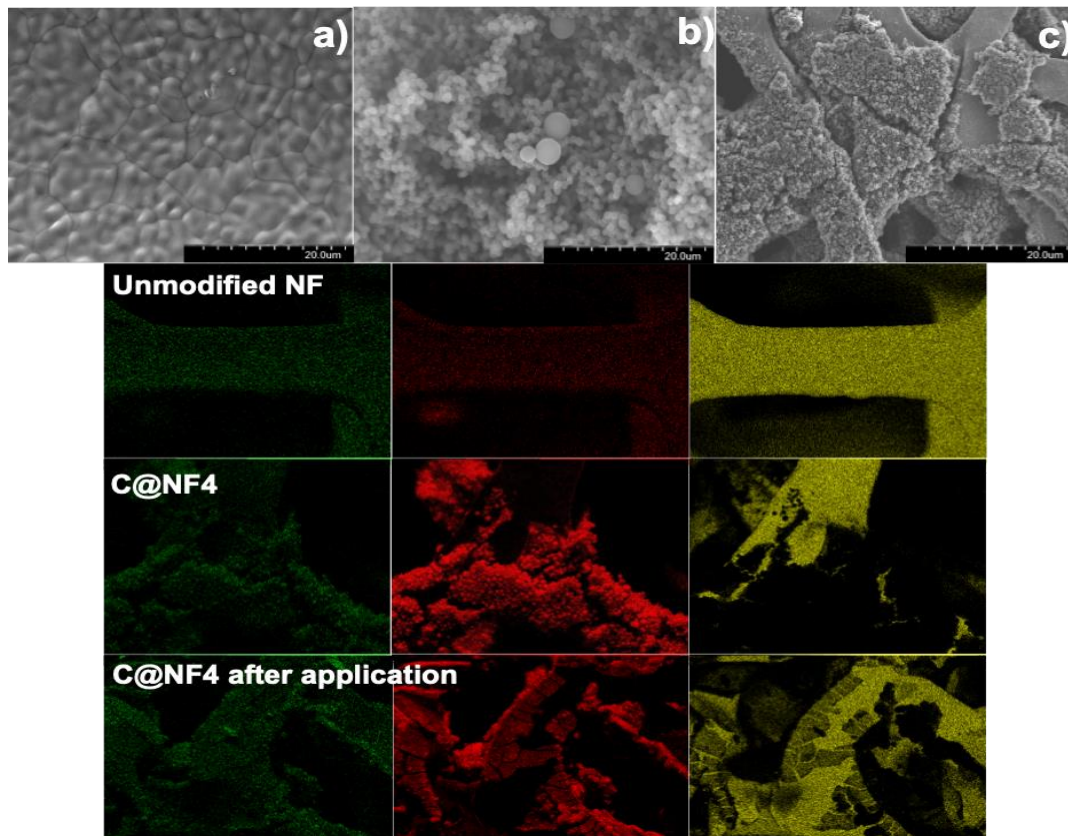


Figure 3. SEM-EDS mapping of Oxygen (green dots), carbon (red dots), and nickel (yellow dots) characteristics of a) unmodified Nickel foam electrodes, b) C@NF4, and c) C@NF4-after sensor applications

3.2. Preliminary Electrochemical Study of C@NF4

Cyclic voltammetry of C@NF4 was conducted for a $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ solution to determine electrochemical active surface area (ECSA).

ECSA was calculated by plotting I_p vs $v^{1/2}$ using the Randles-Sevcick equation as follows:

$$I_p = (2.69 \times 10^5).n^{3/2}.D^{1/2}.C.A.v^{1/2} \quad (1)$$

with I_p as current peak, n as number of electrons transferred in redox event, D as diffusion coefficient, C as concentration, A as electrochemical active surface area and v as root scan rate. The calculated ECSA is approximately 0.02361 cm^{-2} which is greater than the unmodified nickel foam electrode (0.00179 cm^{-2}). The existence of carbon material with specific spherical structure can increase electrochemical active surface area that enhances conductivity of prepared electrodes (Duraisamy et al., 2022; Kong et al., 2010). It proclaims that the surface enhancement has successfully increased the electrochemical behavior of material using combination hydrothermal-carbonized methods.

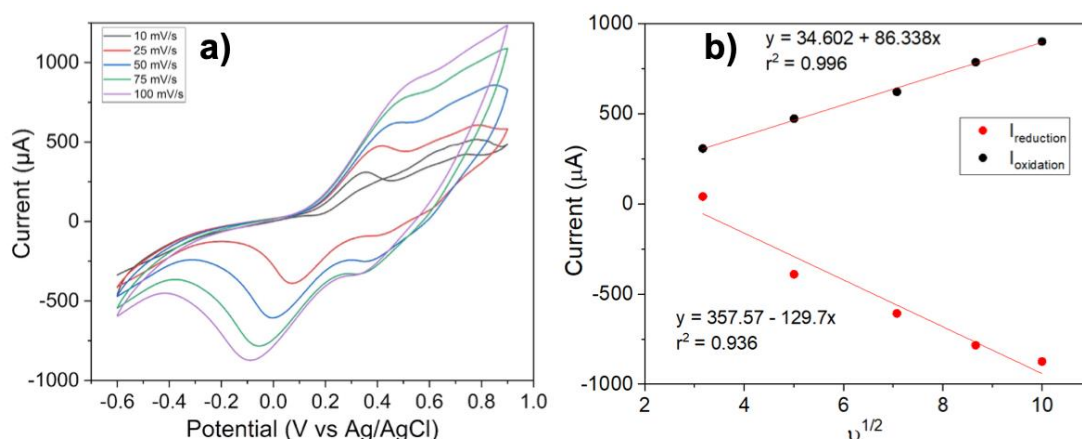
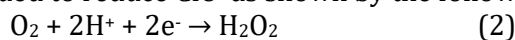


Figure 4. a) Voltammogram of 1 mM $K_3(FeCN)_6$ in 0.1M PBS pH 6.0 at C@NF4 electrode and b) Their related plots of the oxidation and reduction peak currents vs the potential

3.3. Performance of C@NF4 for HOCl detection

The detection of HOCl at C@NF4 was studied by using cyclic voltammetry and amperometry techniques. Figure 5.a shows the comparison of the voltammograms 2 µg/L HOCl in 0.1M PBS pH 6.0, suggesting that the presence of a carbon layer on the surface of the nickel foam electrode can increase the current response of the similar electrochemical reactions. The highest reduction current of HOCl at -0.3 V (vs. Ag/AgCl) was observed. Inset of Figure 5.a. shows the current response of unmodified NF electrode at the potential of -0.3 V was around 10 µA. This current was significantly increased to 300 µA when using the C@NF4 electrode. This result indicate the developed electrode can catalyze the reduction process of OCl⁻ to be Cl⁻ species on the surface electrode (Rahmawati et al., 2022; Silmi et al., 2018). Watanabe et al. (2016) proposed that the reduction reaction of HOCl was initiated by the formation of H₂O₂, which then continued to reduce OCl⁻ as shown by the following reaction:



Since HOCl partially dissociated, the reduction process will take place based on the following reaction (Watanabe et al., 2016):



This reaction also explains that the concentration of H⁺ can affect the current responses. Accordingly, the current responses in different pH solutions were investigated. Figure 5.b shows the higher pH than 6.0 reduces the current responses since the presence of OCl⁻ in the system decreases as the pH increases. On the contrary, an excess of H⁺ will react with OCl⁻ in the system causing a shift in the equilibrium to the reactant (Kaur et al., 2020; Nizer et al., 2020). However, the current response was slightly increased at pH 8 compared to the pH 7, caused by the presence of more OH⁻ species (base atmosphere) generating the formation of H₂O₂ to catalyze the reduction reaction of HOCl depicted by the increasing signal to background ratio than pH 7 (Figure 5.b) (Syukur et al., 2023). Based on this result, pH 6.0 was selected for the next experiments.

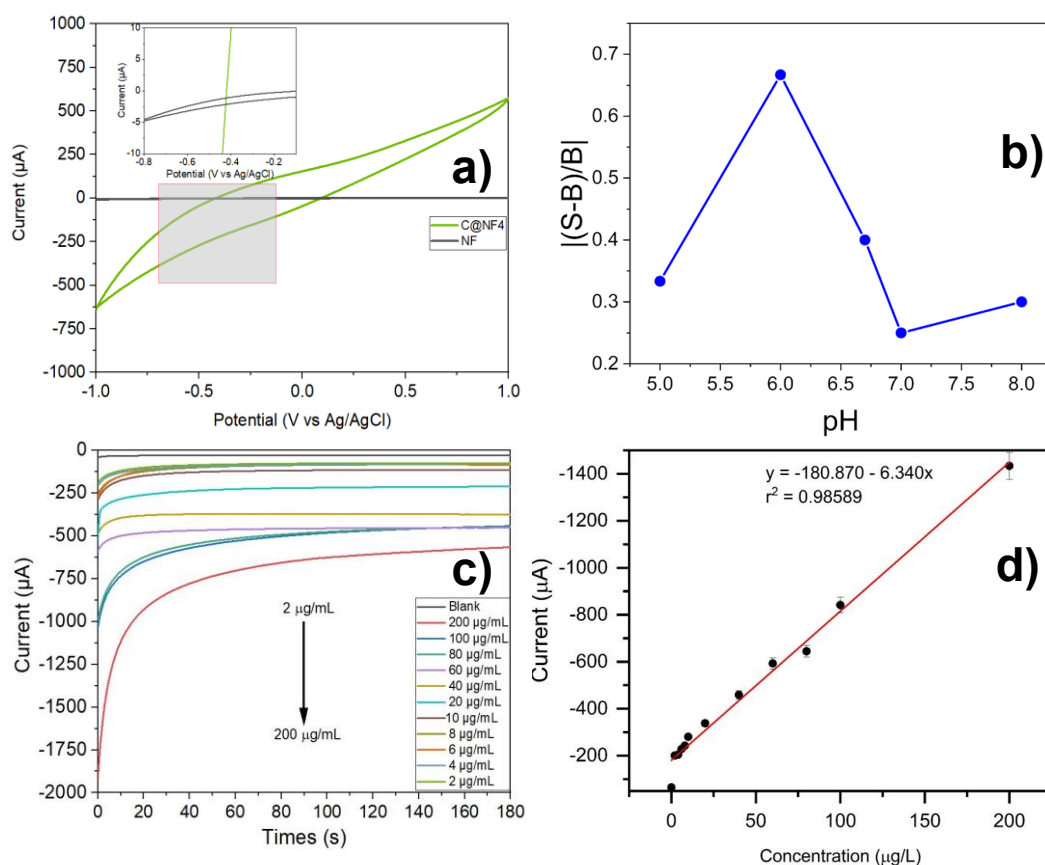


Figure 5. a) Voltammogram of $2\mu\text{g/L}$ HOCl in 0.1M PBS pH 6.0 at the unmodified NF and at C@NF4 electrode, b) The dependence of the current responses of the voltammograms using C@NF4 on the pH solutions, c) Amperometry responses of various concentrations of HOCl (from $2.0\mu\text{g/L}$ to $200.0\mu\text{g/L}$) using C@NF4 at an applied potential of -0.3 V (vs. Ag/AgCl), and d) Its linearity curve. The inset of (a) showing the magnification of the voltammograms

At the optimum pH of 6.0, the linear correlation between various concentrations of HOCl was determined using amperometry technique. A fixed potential of -0.3 V was applied for 180 seconds with 0.1 M PBS pH 6.0 as the electrolyte. The amperograms are shown in Figure 5.c, while the linear plots are displayed in Figure 5.d. Good linearity ($R = 0.99$) can be achieved with the linear equation of the linearity equation $I(\mu\text{A}) = -180.730[\text{HOCl}] + 6.340$ in the concentration range from $2\mu\text{g/L}$ to $200\mu\text{g/L}$.

The performance of electrodes was examined by LOD (limit of detection) and LOQ (limit of quantification) using the formula below:

$$\text{LOD} = 3 \times \text{SD} / b \quad (5)$$

$$\text{LOQ} = 10 \times \text{SD} / b \quad (6)$$

where SD is the standard deviation and slope (b) of the regression line.

Using Equation 4 and 5, the developed sensor achieved LOD down to $1.96\mu\text{g/L}$ and LOQ = $6.53\mu\text{g/L}$ with sensitivity of $9.112\text{ mA}/\mu\text{g/L}$.

The stability study of HOCl sensor was performed using C@NF4 as the electrode. The repeatability test with 5 repetitions of sensor measurements was conducted to evaluate the sensor performance in the detection HOCl species using electrochemical detection, showing an RSD of 2.499 %. Meanwhile, the selectivity of the developed sensor was evaluated using interference study with (1:1) v/v ratio of 5 mM Fe^{2+} and 2 mM Cu^{2+} as interference species. Figure 6.a shows that RSD of both species was under 5%, indicating less interference of the HOCl detection.

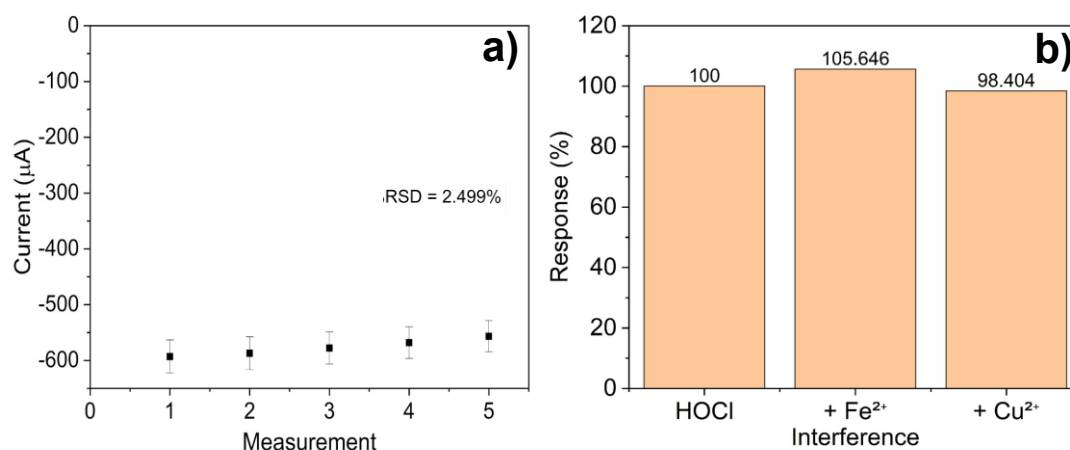


Figure 6. a) Interference study of HOCl detection in the presence of Fe²⁺ and Cu²⁺ as the interferences; b) Repeatability tests at 5 repetitions using amperometric method in HOCl 50µg/L in 0.1M PBS pH 6.0 using C@NF4 at an applied potential of -0.3 V

In order to evaluate the performance of the electrodes, the application to determine the concentration of HOCl in tap water sample was conducted. The results were compared to the conventional detection with UV-Vis spectrophotometry method using the same sample to validate the developed sensor. Based on Table 2, the developed method using amperometry technique demonstrated satisfactory performance in HOCl detection in the tap water sample with percent recovery of 110%. These excellent results were contributed by the surface enhancement of nickel foam using carbon sphere material which not only increase the current response but also increase the electrochemical active surface area and control the stability reaction on the electrode surface (Duraismy et al., 2022; Kong et al., 2010; Sanetuntikul et al., 2014).

Table 2. Application of the prepared electrode to detect HOCl in tap water sample

Methods	Concentration	Detected	%Recovery
Amperometry	3 µg/L	3.30 µg/L	110 %
UV-Vis	3 µg/L	2.95 µg/L	98.3 %

In addition, comparison of the performance with other reported detection methods, such as fluorescence, flow injection analysis, as well as other electrochemical methods (CV, LSV, and CA) is presented in Table 3. The use of electrochemical methods using chronoamperometry technique with C@NF4 as the working electrode shows lower detection limits compared to the use of other detection methods. This is implying that the use of electrochemical methods has been proven to generate higher conductivity with a low detection limit and high sensitivity. Further, the synthesized C@NF4 electrode also shows lower detection limit compared to other carbon-based electrodes, such as graphite electrodes and Polydopamine@electrochemically reduces graphene oxide, indicating that the existence of carbon material with a specific spherical structure increases the electrochemical active surface area and further enhances the conductivity of the proposed electrode. Besides, compared to Ag- and Au- based electrodes, this C@NF4 also shows a better detection performance suggesting that this developed sensor has a good potential for the HOCl detection in environmental application.

Table 3. Comparison of different reported methods for the detections of HOCl

Methods	Detection Limit ($\mu\text{g/L}$)	Linearity Range ($\mu\text{g/L}$)	Sensitivity	Ref
Flow Injection Analysis	1.2×10^5	$0.4 - 7.89 \times 10^5$	-	(Soto et al., 2008)
Fluorescence Molecular Probes	52.08	74.4 - 669.6	-	(Sun et al., 2014)
Ratiometric Fluorescence Molecular Probes	5.95	148.8 - 744	-	(Jia & Ma, 2011)
Electro-chemiluminescence	65.47	$0.07 - 3720 \times 10^3$	$18.56 \text{ a.u. } \mu\text{M}^{-1} \text{ cm}^{-2}$	(Rahmawati et al., 2022)
Electrochemical - LSV (Inkjet Printed Silver)	2.98	$1 - 100 \times 10^3$	$30 \mu\text{C/ppm}$	(Jović et al., 2015)
Electrochemical - CV (PDA@ERGO-GC*)	3.27	$0.73 - 16.01 \times 10^3$	$0.0071 \text{ uA } \mu\text{M}^{-1}$	(Kumar et al., 2017)
Electrochemical - LSV (Graphite electrode)	1443.34	$1.45 - 435.24 \times 10^3$	-	(Pathiratne et al., 2008)
Electrochemical - CA (MnTAPP-nano Au/GCE**)	1785.50	$1.78 - 796.08 \times 10^3$	-	(Thiagarajan et al., 2011)
C@NF4	1.96	2 - 200	$9.112 \text{ mA}/\mu\text{g/L}$	This work

*Polydopamine@electrochemically reduced graphene oxide

**Poly manganese tetra (o-amino phenyl) porphyrin (MnTAPP)-nano Au film

4. Conclusions

A surface enhancement of nickel foam-based electrode using carbon material has been successfully developed by hydrothermal-carbonization method. The modification method produced carbon layer with the specific spherical structure confirmed using SEM-EDS mapping characterization showing the optimum condition of carbonized method was achieved at 4th carbonized cycles (C@NF4) with the carbon element content of more than 90%. The Raman spectroscopy confirmed the formation of graphitic materials as shown by a couple Raman shift of carbon at around 1352 cm^{-1} and 1597 cm^{-1} with ID/IG ratio 0.74. The developed material was successfully performed as a non-enzymatic sensor of HOCl using amperometry techniques at an applied potential of -0.3 V (vs. Ag/AgCl) in 0.1 M phosphate buffer solution pH 6.0 with good sensitivity and linearity. This sensor also shows good selectivity in the presence of interference compounds such as FeCl_2 and CuSO_4 with ratio (1:1) v/v. The use of the developed methods for the hypochlorite ions measurement in tap water has been validated with the UV-VIS method. Therefore, the stability of carbon layer formation on the nickel foam substrate still needs to be improved using catalyst ink like Nafion which can maintain the surface reaction and to discover another promising sample treatment to increase the selectivity towards the real sample detection.

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Author Contribution

ARS and HGR: Conceptualization, data curation, formal analysis, and writing the original draft. IR, YT, and YMTAP.: Analysis, validation, writing – review and editing. DN: Data

curation and formal analysis. ARSES and YKK: validation, funding acquisition, and supervisor.

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Conflicts of Interest

The authors declare no conflict of interest.

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