

Polypyrrole (PPy) is a versatile conducting polymer with exceptional electrical conductivity, stability, and ease of synthesis, making it a promising material for applications in sensing, energy conversion and storage. In this study, we investigate the influence of electrodeposition duration on the thickness, morphology, and electrochemical properties of PPy layers deposited on nickel foam (NF). Electropolymerization was performed via chronopotentiometry, using nickel foam as the working electrode in a pyrrole/ NaClO_4 electrolyte solution at a constant current density of $40 \text{ mA} \cdot \text{cm}^{-2}$. Deposition times of 30, 60, and 120 seconds were explored to optimize the deposited PPy layer on NF.

The structural, morphological, and electrochemical properties of the PPy-modified NF electrodes were systematically characterized using a range of physicochemical techniques. Among the tested deposition times, The PPy/NF-60 electrode exhibited high sensitivity, with values of $2540 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ and $1310 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ across wide linear ranges of $10\text{--}1000 \mu\text{M}$ and $1000\text{--}8000 \mu\text{M}$, respectively. The enhanced electrocatalytic performance of the PPy/NF composite can be attributed to the synergistic effect between nickel foam and PPy. Nickel foam provides a high surface area and excellent electrical conductivity, while PPy contributes to the electrocatalytic activity and selectivity for ascorbic acid detection. These findings highlight the potential of PPy/NF composites as high-performance electrochemical sensors for ascorbic acid and other biomolecules.

Keywords: Polypyrrole (PPy), Nickel foam (NF), Electrochemical sensing, Ascorbic acid detection, Electrodeposition, Synergistic effect.

INTRODUCTION

Vitamin C is a water-soluble antioxidant known for its regenerative and anti-cancer properties. While several analytical methods such as titration, spectrophotometry, and chemiluminescence exist for detecting AA, many are time-consuming and can lead to AA degradation. Electrochemical detection offers a promising alternative but is hindered by AA's high oxidation potential and surface fouling of electrodes. To overcome these challenges, researchers have developed chemically modified electrodes to enhance sensitivity and selectivity. Among various materials, PPy has gained attention due to its excellent conductivity, biocompatibility, and ease of synthesis. Its integration with flexible substrates also opens new possibilities for wearable and implantable AA sensors.

This study aims to develop a new electrode material (PPy-NF) in case to create a novel nonenzymatic Ascorbic acid biosensors witch can be effectively employed in detecting Ascorbic acid with a good sensibility and wide linear ranges.

SYNTHESIS

Distilled pyrrole was introduced into a 0.2 M NaClO_4 solution at a ratio of **1 part Py to 15** parts solution by volume within an electrolytic cell. NF served directly as the working electrode, maintained at a current of 40 mA in the Py/NaClO_4 solution. Electropolymerization of Py occurred using a three-electrode electrochemical workstation (Metrohm Autolab PGSTAT128N Potentiostat/Galvanostat), with a Pt wire and SCE employed as the counter and reference electrodes, respectively. The typical electropolymerization duration is 30, 60 and 120 seconds for each electrode. Following the electropolymerization process, the PPy/NF underwent rinsing with water and air-dried to obtain the final product.

RESULTS AND DISCUSSIONS

The SEM images in **Fig. 1** illustrate the progressive morphological evolution of the electrodes as a function of Py deposition time on NF structure :

Fig. 1a, b and c displays SEM micrographs of the nickel foam used as a substrate, revealing a 3D porous and interconnected skeletal structure with a smooth surface morphology.

Fig.1d-j After 30 seconds of electrodeposition, the NF structure exhibits an initial PPy layer characterized by partial surface coverage, with regions of the underlying nickel foam still exposed. Discrete polypyrrole aggregates are observed as scattered nodular formations, indicating the onset of nucleation and early-stage growth.

Fig.1e-h After 60 seconds of deposition, the polypyrrole layer becomes more continuous and denser, covering a larger portion of the NF surface. The deposited PPy forms more numerous and larger structures, resulting in a rougher and more compact surface texture.

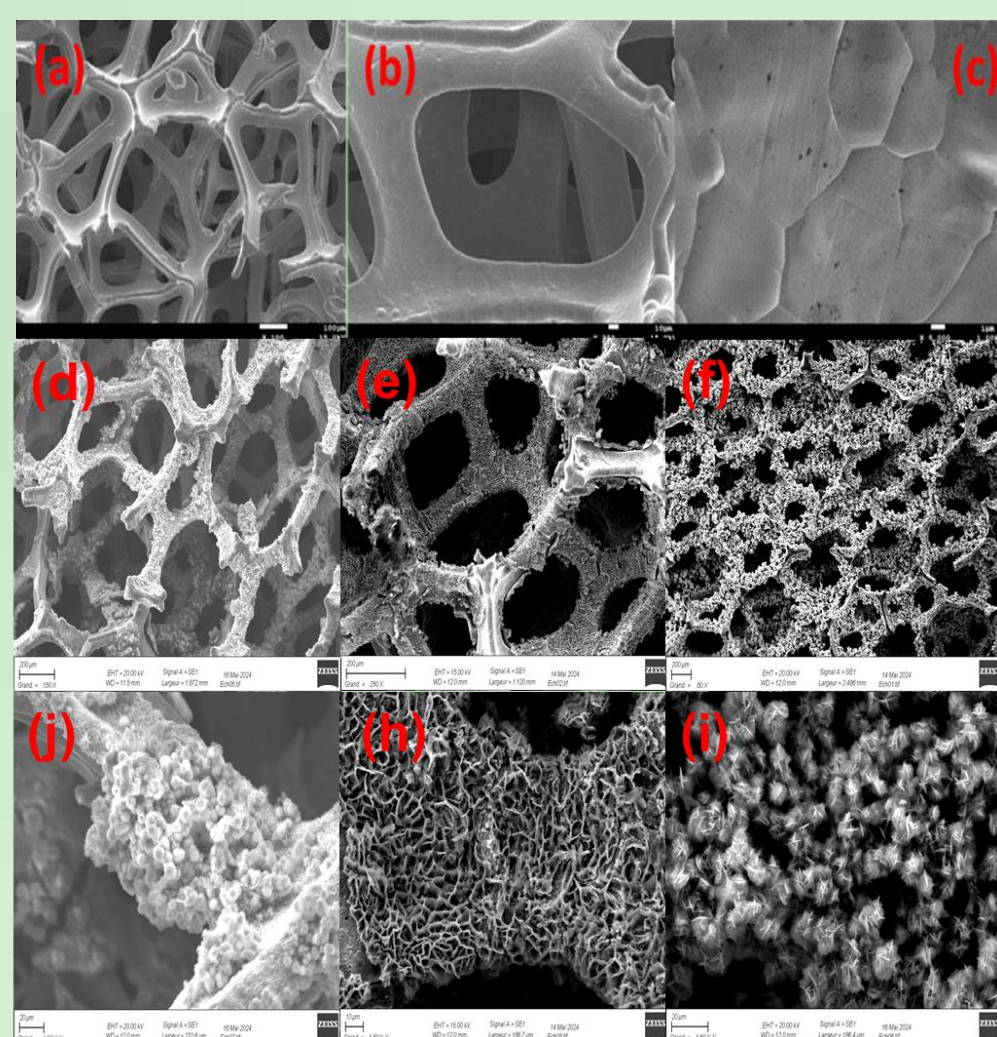


Fig1: High- and low-magnification SEM images of electrodes prepared at different polypyrrole deposition durations: (a, b and c) 0s, (e-h) 30s, (f-i) 60s and (j-g) 120s.

Fig.1f-i At 120 seconds of deposition, the NF scaffold is nearly fully coated with polypyrrole, exhibiting a dense and homogeneous film. Well-defined and uniformly distributed PPy clusters cover the surface, suggesting a complete and uniform growth of the conducting polymer layer.

RESULTS AND DISCUSSIONS

To elucidate the synergic effect between the PPy foam and the Nickel foam heterostructure regarding the Ascorbic acid sensing; electrochemical assessment of the fabricated electrodes was conducted using an electrochemical workstation equipped with a three-electrode configuration. The fabricated electrodes served as the working electrode, while SCE and platinum foil were employed as the reference and counter electrodes, respectively, when Electrochemical cell is filled with PBS tompon solution, The working electrode is totally binder-free having a functional geometric area of 1 Cm^2 .

Fig.3 presents the cyclic voltammograms of the **PPy/NF-60** electrode recorded at different A.A concentrations, with a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$.

As the concentration of A.A increases, the anodic peak current density rises significantly. A well-defined oxidation peak appears around 0.6 V vs. SCE , Therefore, this potential was selected as the optimal working potential for the electrode, as it allows efficient A.A oxidation while avoiding significant competition of water oxidation evolution reaction (OER).

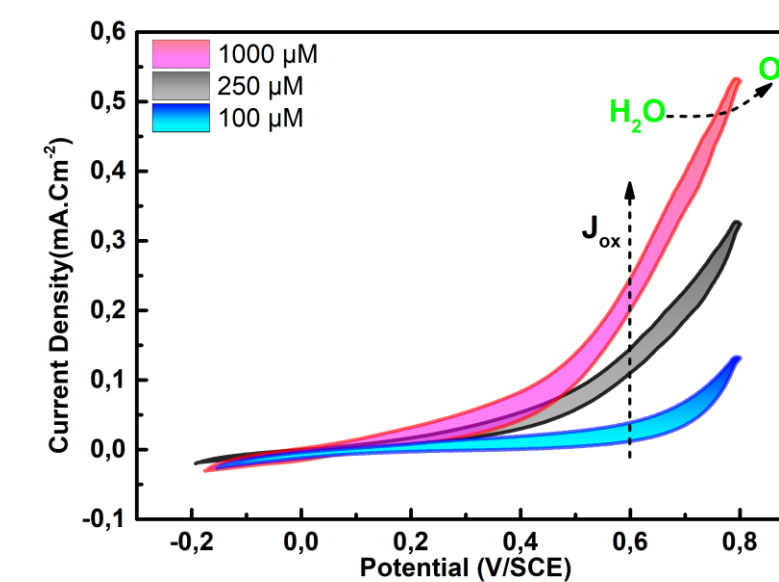


Fig3: Voltammograms recorded at different (A.A) concentrations for the PPy/NF-60 electrode.

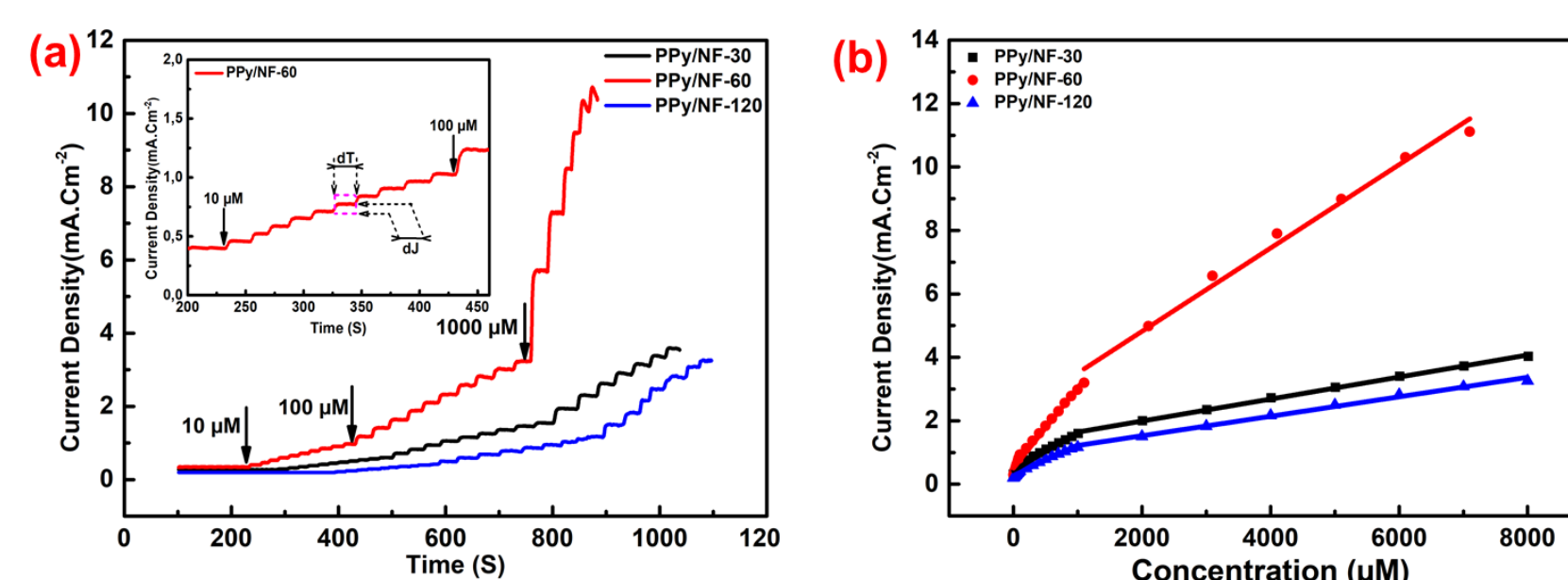


Fig4: (a) Chronoamperometric response of electrodes; (b) Corresponding calibration curves obtained of each electrode.

Fig.4.a : The amperometric responses of the different PPy/NF electrodes were recorded at an applied potential of 0.6 V vs. SCE . Upon successive additions of ascorbic acid ranging from $10 \mu\text{M}$ to $8000 \mu\text{M}$, all current–time (i–t) curves exhibited a stepwise increase in current density, with clear differences observed among the various electrodes. Notably, the oxidation current of ascorbic acid was found to be higher and more stable for the electrodes prepared with **60 s** PPy deposition time.

Fig.4.b : presents the linear fitting of the amperometric response (current density) as a function of A.A concentration. For the different electrodes, two distinct linear ranges were identified: from 10 to $1000 \mu\text{M}$ and from 1000 to $8000 \mu\text{M}$. The corresponding linear regression equations are listed in Table.1, The electrodes prepared with **30 s** and **120 s** deposition durations showed nearly identical amperometric responses. However, stay at **60 seconds** deposition time led to a significant increase in (A.A) oxidation current, indicating that the optimal deposition duration is **60 seconds**.

Tab.1. Linear fitting parameters of the different PPy/NF electrodes at a working potential of 0.6 V vs. SCE

Electrode	from 10 to $1000 \mu\text{M}$	from 1000 to $8000 \mu\text{M}$
PPy/NF-30	$J = 1230 C_{AA} + 421$; $R^2 = 0.990$	$J = 347 C_{AA} + 1295$; $R^2 = 0.999$
PPy/NF-60	$J = 2540 C_{AA} + 511$; $R^2 = 0.993$	$J = 1310 C_{AA} + 2190$; $R^2 = 0.994$
PPy/NF-120	$J = 965 C_{AA} + 272$; $R^2 = 0.992$	$J = 307 C_{AA} + 911$; $R^2 = 0.997$

A high sensitivity of $2540 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ was recorded for (A.A) concentrations ranging from 10 to $1000 \mu\text{M}$. Moreover, the electrode maintains a significant sensitivity of $1310 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ over a wider concentration range of 1000 to $8000 \mu\text{M}$.

This difference may be attributed to optimal PPy nucleation on the nickel surface, which results in the formation of abundant active sites. These facilitate the accessibility of the ascorbic acid molecules to the catalytic sites and promote rapid oxidation kinetics, whereby the reaction products quickly vacate the active sites, enabling their reusability.

CONCLUSION

In summary, a new electrode material, PPy-NF has been successfully developed for creating nonenzymatic (A.A) biosensors with a good sensibility and wide linear ranges. Compared to other previously reported (A.A) electrochemical sensors, this sensor benefits from the combined effects of PPy foam and Nickel foam. This synergy enhances the establishment of an efficient electron pathway and simultaneously reduces the distance of electron transport. Moreover, PPy aids in enhancing the conductivity of the electrode, improving its electrocatalytic activity toward (A.A). Upon electrochemical tests, The **PPy/NF-60** electrode exhibited high sensitivity, with values of $2540 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ and $1310 \mu\text{A} \cdot \text{mM}^{-1} \cdot \text{cm}^{-2}$ across wide linear ranges of $10\text{--}1000 \mu\text{M}$ and $1000\text{--}8000 \mu\text{M}$, respectively. Consequently, there is significant promise for PPy/NF-60 sensing electrode to be utilized in accurately determining (A.A) concentration in real clinical samples.

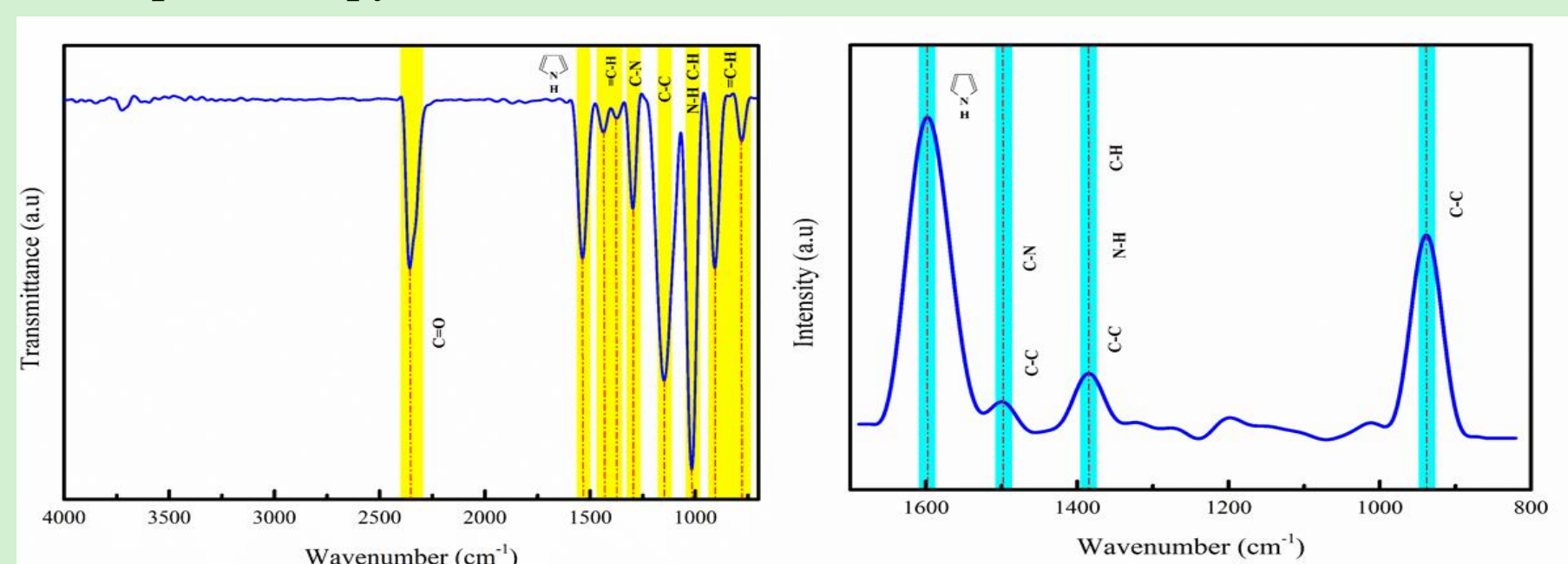


Fig2:(a) FTIR spectrum and **(b)** Raman spectrum of the PPy foam

The FTIR spectrum shows characteristic peaks of PPy, including pyrrole ring vibrations at 1544 cm^{-1} , C–N and C–C stretching around 1290 and 1149 cm^{-1} , and deformation modes of C–H and N–H bonds at 1035 cm^{-1} . Similarly, the Raman spectrum displays key PPy signals, such as the C=C and C–N stretching bands at 1570 and 1360 cm^{-1} .

These spectral features confirm the successful polymerization of polypyrrole on the electrode surface.