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Article

Green-Mediated Synthesis of NiCo₂O₄ Nanostructures Using Radish White Peel Extract for the Sensitive and Selective Enzyme-Free Detection of Uric Acid

Abdul Ghafar Solangi ¹, Aneela Tahira ¹, Baradi Waryani ⁹, Abdul Sattar Chang ², Tajnees Pirzada ¹, Ayman Nafady ⁵, Elmuez A. Dawi ⁸, Lama M. A. Saleem ⁷, M. Padervand ⁷, A. Haj Ismail ⁸, Kangle LV ⁹, Brigitte Vigolo ⁶ and Zafar Hussain Ibupoto ^{2,*}

¹ Institute of Chemistry, Shah Abdul Latif University Khairpur Mirs, Khairpur Mirs 66111, Sindh, Pakistan; ghaffarchemistry786@gmail.com (A.G.S.); aneela.tahira@salu.edu.pk (A.T.); tajnees@salu.edu.pk (T.P.)

² Institute of Chemistry, University of Sindh, Jamshoro 76080, Pakistan; asattar.chang@usindh.edu.pk (A.S.C.)

³ Department of Fresh Water Biology and Fisheries, University of Sindh, Jamshoro, Sindh, Pakistan; baradiw@usindh.edu.pk

⁴ Department of Chemistry, Faculty of Science, University of Maragheh, Maragheh P.O. Box. 55181-83111, Iran; padervand@maragheh.ac.ir

⁵ Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; anafady@ksu.edu.sa

⁶ Institut Jean Lamour, Université de Lorraine, CNRS, IJL, F-54000 Nancy, France; brigitte.vigolo@univ-lorraine.fr

⁷ Biomolecular Science, Earth and Life Science, Amsterdam University, De Boelelaan 1105/1081, HV Amsterdam, The Netherlands; lamysaleem@gmail.com

⁸ Nonlinear Dynamics Research Centre (NDRC), Ajman University, Ajman P.O. Box 346, United Arab Emirates; e.dawi@ajman.ac.ae (E.A.D.); a.hajismail@ajman.ac.ae (A.H.I.)

⁹ College of Resource and Environment, South-Central Minzu University, Wuhan 430074, China; lvkangle@mail.scuec.edu.cn

* Correspondence: zaffar.ibhupoto@usindh.edu.pk

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Abstract: The ability to measure uric acid (UA) non-enzymatically in human blood has been demonstrated through the use of a simple and efficient electrochemical method. A phytochemical extract from radish white peel extract improved the electrocatalytic performance of nickel–cobalt bimetallic oxide (NiCo₂O₄) during a hydrothermal process through abundant surface holes of oxides, an alteration of morphology, an excellent crystal quality, and increased Co(III) and Ni(II) chemical states. The surface structure, morphology, crystalline quality, and chemical composition were determined using a variety of analytical techniques, including powder X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), and X-ray photoelectron spectroscopy (XPS). The electrochemical characterization by CV revealed a linear range of UA from 0.1 mM to 8 mM, with a detection limit of 0.005 mM and a limit of quantification (LOQ) of 0.008 mM. A study of the sensitivity of NiCo₂O₄ nanostructures modified on the surface to UA detection with amperometry has revealed a linear range from 0.1 mM to 4 mM for detection. High stability, repeatability, and selectivity were associated with the enhanced electrochemical performance of non-enzymatic UA sensing. A significant contribution to the full outperforming sensing characterization can be attributed to the tailoring of surface properties of NiCo₂O₄ nanostructures. EIS analysis revealed a low charge-transfer resistance of 114,970 Ohms that offered NiCo₂O₄ nanostructures prepared with 5 mL of radish white peel extract, confirming an enhanced performance of the presented non-enzymatic UA sensor. As well as testing

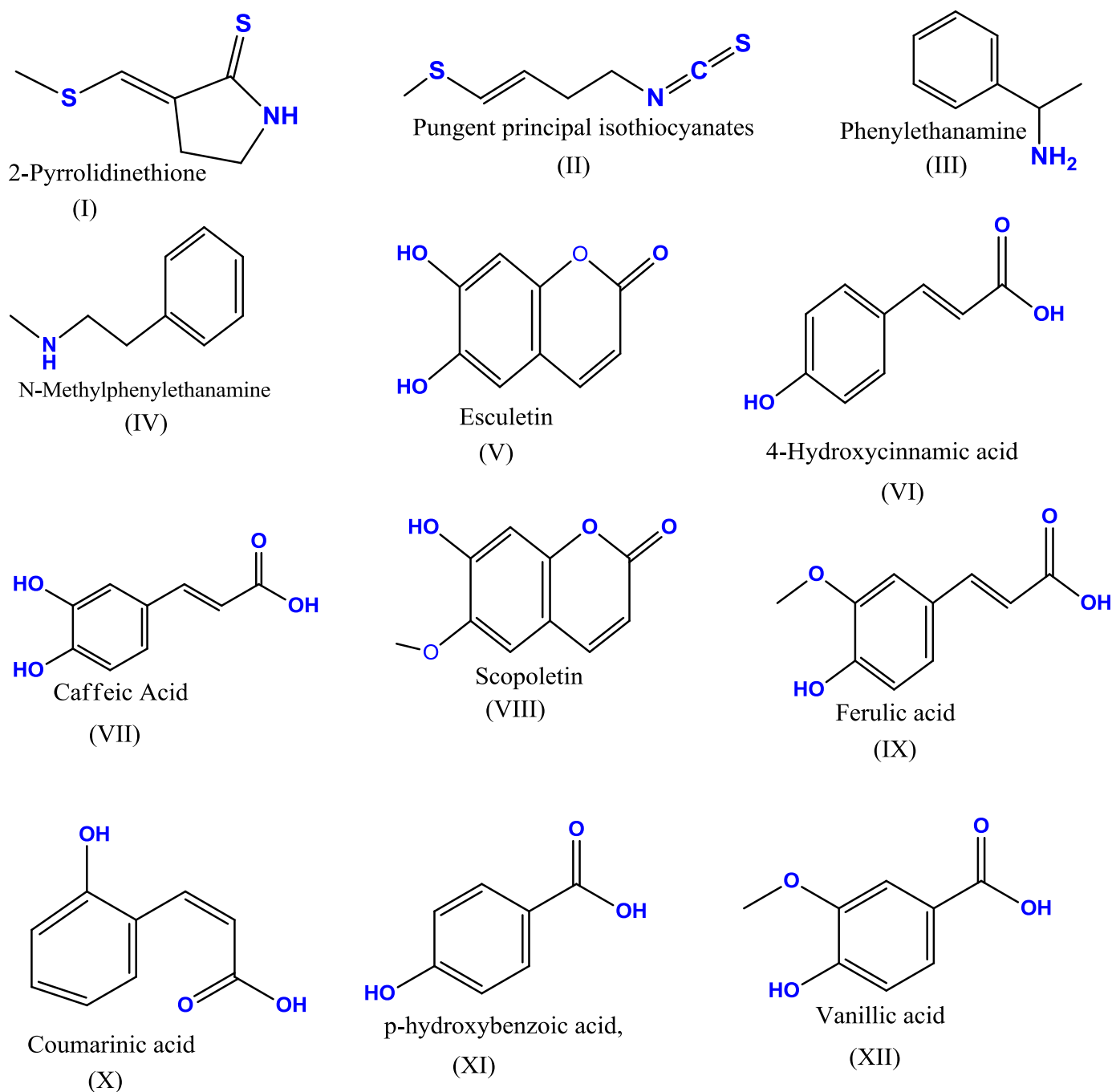
the practicality of the UA sensor, blood samples from human beings were also tested for UA. Due to its high sensitivity, stability, selectivity, repeatability, and simplicity, the developed non-enzymatic UA sensor is ideal for monitoring UA for a wide range of concentrations in biological matrixes.

Keywords: non-enzymatic uric acid sensor; phytochemicals; radish white peel extract; biological matrix

1. Introduction

A purine-based compound called alkaloids is used by our bodies to produce uric acid (UA) [1,2]. UA concentrations in serum samples range between 0.13 and 0.46 mM, whereas UA concentrations in urine samples range between 1.49 and 4.50 mM [3]. An abnormal level of UA in the human body is associated with several chronic and life-threatening diseases, including preeclampsia, arthritis, renal dysfunction, cardiovascular disease, obesity, high blood pressure, and kidney disease [4–7]. An increase in UA levels in blood serum has been identified as a major cause of cardiac disease [8]. For this reason, it is essential to measure and monitor UA in order to prevent the onset of dangerous conditions and to reduce the risk of premature death. Several analytical methods have been developed to measure UA as a result of this high importance, including colorimetric enzymatic tests [9]. Capillary electrophoresis method [10], surface-enhanced Raman scattering [11], liquid chromatography [12], electrochemical method [13], fluorescence spectroscopy [14], and chemiluminescence [15] are among the methods used. It is common for these analytical methods to be extremely expensive, time-consuming, and complex to operate. However, electrochemical methods are inexpensive, sensitive, and selective, thus they have been extensively studied [16–21]. A number of electrochemical approaches have been used to quantify UA's high electrooxidation properties, including enzyme-based and enzyme-free methods [22–26]. Due to the high costs associated with enzyme immobilization and denatured issues with uricase enzyme during storage, non-enzymatic approaches have become increasingly popular as alternatives to enzyme-based approaches [27]. In non-enzymatic approaches, highly electrocatalytic materials are always desirable [18,16]. To realize non-enzymatic UA sensors quickly, it will be increasingly necessary to develop new materials with tailored surfaces that outperform electrocatalytic properties. This task, however, appears to be challenging because novel materials with tailored surfaces do not possess electrocatalytic properties. For the development of highly catalytic materials for non-enzymatic UA sensors, several challenges must be overcome, such as poor electrical conductivity, a limited number of catalytic sites, and chemical stability concerns. Therefore, numerous electrocatalytic materials have been developed and investigated for the development of non-enzymatic sensors [28–31]. A significant electrochemical activity of metal oxides makes them potentially suitable for this application [32–34]. As a result of its high electrical conductivity and favorable redox properties, a bimetallic oxide, particularly nickel–cobalt oxide (NiCo_2O_4), has been identified as a potential candidate for the development of non-enzymatic sensors. As NiCo_2O_4 nanostructures exhibit poor electrochemical performance due to their limited surface properties, they have been utilized in composites with other nanostructured materials, such as $\text{Fe}_2\text{O}_3 @ \text{NiCo}_2\text{O}_4$ [35], $\text{MnO}_2/\text{NiCo}_2\text{O}_4$ [36], $\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$ [37,38], and $\text{NiCo}_2\text{O}_4 @ \text{graphene}$ [39]. It has been observed that composite NiCo_2O_4 systems exhibit enhanced charge transfer between electrode and analyte. Several morphologies of NiCo_2O_4 have been prepared, including nanotubes [37], nanorods [36], nanospheres [35], and nanosheets [33]. In spite of NiCo_2O_4 's diverse architecture, however, the material fails to perform as expected [35,36,38]. As a result, it is imperative to identify new strategies for improving the elec-

trochemical performance of NiCo₂O₄ in order to develop more sensitive non-enzymatic UA sensors. Recent years have seen a great deal of interest in green chemistry due to its simplicity, eco-friendliness, low cost, and environmental friendliness [39–42]. Several natural products obtained from biomass wastes can be used to tailor the surface properties of nanostructured materials, including catalytic sites and charge transfer properties [41,42]. Only a few studies have been conducted on the synthesis of NiCo₂O₄ nanostructured materials from biomass wastes. The present study examines for the first time the effect of radish white peel extract (*Raphanus sativus*) on the morphology, crystal defect, and surface properties of NiCo₂O₄ that will be used for fabricating a non-enzymatic UA sensor. Radish white peel extract contains a wide range of phytochemicals, including alkaloids, glucosinolates, phenolic compounds, organic acids, anthocyanins, and isothiocyanates. [40,41] (Scheme 1).



Scheme 1. The various phytochemicals present in the radish (*Raphanus sativus*) peel extract.

The radish white peel extract possesses major phytochemicals, like as 4-hydroxycinnamic acid, caffeic acid, ferulic acid, and isothiocyanates, which were used as stabilizing, capping, and reducing agents, and played a significant role toward enhanced electrochemical properties of NiCo₂O₄ nanostructures.

In this study, we have used radish white peel extracts for the surface engineering of NiCo₂O₄ nanostructures by hydrothermal methods. The volume of extracts from peels was examined in order to determine the ideal concentration at which NiCo₂O₄ nanostructures could be scaled up for high performance production. An extensive linear range of UA detection was detected using surface-modified NiCo₂O₄ nanostructures ranging from 0.1 mM to 8 mM.

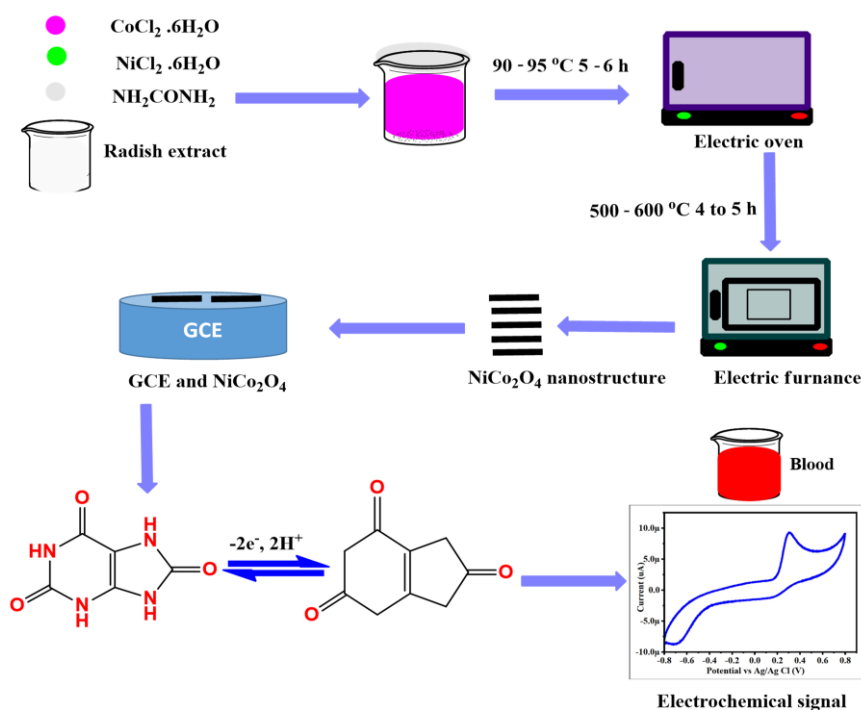
2. Experimental Section

2.1. Chemicals Used

In this study, cobalt chloride hexahydrate (CoCl₂·6H₂O), nickel chloride hexahydrate (NiCl₂·6H₂O), glucose, lactic acid, uric acid, sodium chloride, potassium chloride, ascorbic acid, sodium hydroxide, urea, hydrochloric acid, disodium phosphate, and monopotassium phosphate were applied without pretreatment. We obtained all analytical grade chemical reagents from Sigma Aldrich, Karachi, and Sindh Pakistan. UA detection was performed by preparing the desired solutions in deionized water, followed by preparing a buffer solution containing 0.1 M phosphate at pH 7.0 for UA detection.

2.2. Green-Mediated Synthesis of NiCo₂O₄ Nanostructures Using Radish White Peel Extract

A hydrothermal method was used for phytochemical synthesis of NiCo₂O₄ nanostructures. The radish white was purchased, washed with deionized water, and allowed to dry at room temperature prior to the growth process. Small pieces of radish white were chipped after the peel had been removed. An automatic juicer was then used to collect juice from the peel. An extract of the peel was used in the subsequent synthesis of NiCo₂O₄ nanostructures. NiCo₂O₄ nanostructures were prepared using 0.1 M cobalt chloride hexahydrate, 0.1 M urea, and 0.015 M nickel chloride hexahydrate in 100 mL of deionized water through a hydrothermal process. Various amounts of radish white peel extract were used to synthesize NiCo₂O₄ nanostructures. The pH of the precursor solution was 8.2 and 7.1, respectively. Afterward, the growth solutions were sealed with aluminum sheets and grown at 95 °C for five hours. Filter paper was used to collect the bimetallic hydroxide phase, and deionized water was used to wash it several times. The material was then thermally roasted for five hours at 500 °C after drying for 12 h. With the same procedure, pristine NiCo₂O₄ nanostructures were obtained without adding radish white peel extract. An illustration of the synthesis of NiCo₂O₄ nanostructures as prepared can be found in Scheme 2.



Scheme 2. Stepwise synthesis of NiCo₂O₄ nanostructures using radish white peel extract during hydrothermal method, UA detection, and real blood sample analysis.

2.3. Physical Investigations on the Surface-Modified NiCo₂O₄ Nanostructures

An assessment of the morphology of NiCo₂O₄ nanostructures was carried out by scanning electron microscopy (SEM: JEOL Japan Model No. JSM-IT 100, Auto Fine Coater: JEC-3000FC; the coating performed at 20 mA current for 60 s) using an accelerating voltage of 10 kV. We assessed the crystal quality of radish white peel extract-assisted NiCo₂O₄ nanostructures using powder X-ray diffraction (XRD) at 45 kV and 45 mA using CuK radiation ($\lambda = 1.5418 \text{ \AA}$) as an X-ray source. The localized nanoscale structure was studied using high-resolution transmission electron microscopy (HRTEM) at a voltage of 200 kV. Utilizing energy dispersive spectroscopy, we were able to quantify the elemental mapping. The chemical composition of the surface was determined using X-ray photoelectron spectroscopy (XPS) in high vacuum. As a reference binding energy, we calibrated the XPS data using C1s at 284.6 eV and deconvolved the XPS features using a Shirley-type background and Voigt curves.

2.4. Non-Enzymatic Sensing of UA onto Surface-Modified NiCo₂O₄ Nanostructures

A variety of electrochemical methods have been used to characterize the non-enzymatic UA sensor, including cyclic voltammetry, amperometry, electrochemical impedance spectroscopy, and linear sweeping voltammetry. The electrochemical evaluation of NiCo₂O₄ nanostructures was conducted using a three-electrode setup. Three electrodes were used: silver–silver chloride (Ag/AgCl, 3.0 M KCl) as a reference electrode, platinum sheet as a counter electrode, and glassy carbon electrode (GCE) as a working electrode. Prior to modification of the GCE, it was polished with an alumina paste of (0.3 μM) and silicon paper and then cleaned with deionized water. The material ink was prepared by dispersing 10 mg of NiCo₂O₄ nanostructures in 2.5 mL of deionized water and 0.5 mL of Nafion (5%) in 2.5 mL of deionized water. We achieved homogeneous material ink after 15 min of an ultrasonic bath. NiCo₂O₄ nanostructures were applied to the surface of GCE using a drop-cast method. A 10 mM stock solution of UA was pre-

pared in a 0.1 M phosphate buffer solution of pH 7.0. Prior to dissolving the phosphate buffer solution, UA was dissolved in propanol. The selectivity of the non-enzymatic UA sensor was determined with 0.1 mM interfering species, like urea, lactic acid, glucose, ascorbic acid, potassium ions, and sodium ions, in the presence of the same concentration of UA. The linear range of the UA sensor was determined by CV and chronoamperometry methods using various UA concentrations dissolved in 0.1 M phosphate buffer solution (PBS) at pH 7.0. Using this method, it was possible to estimate the low limit of detection of the non-enzymatic sensor [43].

3. Results and Discussion

3.1. Structural and Morphological Investigations of Radish White Peel Extract-Assisted Synthesis of NiCo₂O₄ Nanostructures

In Figure 1a, we show diffraction patterns measured by powder XRD on NiCo₂O₄ nanostructures that reveal their crystal quality. Furthermore, we investigated the effects of phytochemicals present in the white peel extract of radish on the crystal quality of NiCo₂O₄ nanostructures. The reference card number 00-020-0781 confirms that the typical reflections of NiCo₂O₄ nanostructures are well matched with the cubic phase of NiCo₂O₄. The diffraction patterns of NiCo₂O₄ nanostructures have been identified as (111), (220), (311), (222), (400), (511), and (440), respectively, at 19.40, 31.30, 36.880, 38.590, 44.850, 59.410, and 65.300. The morphology of NiCo₂O₄ nanostructures prepared with radish peel extract was examined by SEM. This was performed to compare them with pristine NiCo₂O₄ nanostructures, as shown in Figure 1b–f. NiCo₂O₄ nanostructures with a high degree of heterogeneity exhibit a typical nanorod-like orientation as shown in Figure 1b. Figure 1c–f illustrates that radish white peel extract altered the morphology of NiCo₂O₄ nanostructures toward short-range nanoparticles, confirming the influence of phytochemicals on surface modification. As well as being much smaller in size, nanostructures have a size range between 50 and 100 nm, which is characteristic of nanoparticles. Figure 1f illustrates that radish white peel extract significantly affects the size and morphology of NiCo₂O₄ nanostructures. According to Figure 1f, these phytochemicals determined the morphology and allowed the formation of aggregated and irregularly oriented nanostructures with unfavorable surface properties when 10 mL of radish white peel extract was used during the growth process. A phytochemical from radish white peel extract, shown in Scheme 1, contains oxygenated groups that provide ample coordination with nickel and cobalt metallic ions during the growth process, which results in morphological changes from nanorods to nanoparticles. As-prepared NiCo₂O₄ nanostructures were examined with HRTEM images and Fourier transform (FFT) patterns in order to analyze the deep morphological features and to calculate atomic d-spacing. Figure 2a illustrates that the nanoparticles were assembled in order to form a nanorod-like structure. The HRTEM image shown in Figure 2a confirms the excellent crystallinity of NiCo₂O₄ nanostructures. According to Figure 2b, pristine NiCo₂O₄ nanostructures have a d-spacing of 0.39 nanometers. Using elemental mapping, Figure 2b–d illustrates a uniform distribution of Ni, Co, and O. Figure 2e illustrates the EDS spectrum, which shows Co, Ni, and O as the primary elements. A TEM and HRTEM examination of NiCo₂O₄ nanostructures, as shown in Figure 3a, was conducted along with the calculation of d-spacing. A TEM image revealed typical nanoparticle morphologies, and HRTEM confirmed the high crystal quality of NiCo₂O₄ nanostructures (Figure 3). Figure 3a shows that NiCo₂O₄ nanostructures exhibit a spinel crystal structure and a cubic phase as revealed by the FFT analysis. According to Figure 3b–d, the d-spacing value of this sample was 0.36 nm, in agreement with results published for NiCo₂O₄ nanostructures. An elemental analysis of these nanostructures utilizing 5 mL of radish white peel extract revealed a homogeneous distribution of Co, Ni, and O elements. As shown in Figure 3e, the EDS spectrum indicates that the surface-modified NiCo₂O₄ nanostructures prepared using 5 mL of radish white peel extract contain quantified amounts of Ni, Co, and O.

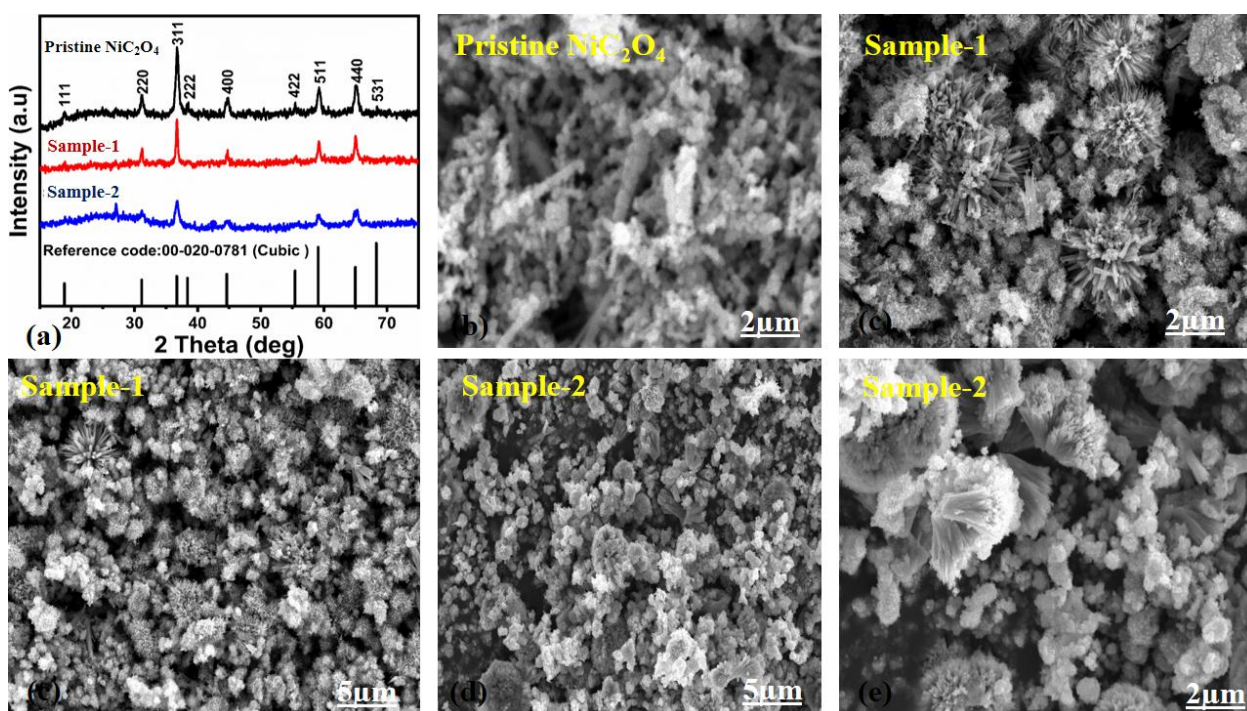


Figure 1. (a) Powder XRD diffraction patterns of pristine, 5 mL, and 10 mL of radish peel extract-assisted NiCo₂O₄ nanostructures, (b-f) Corresponding SEM images of (b) pristine, (c,d) 5 mL, and (e,f) 10 mL of radish peel extract-assisted NiCo₂O₄ nanostructures respectively

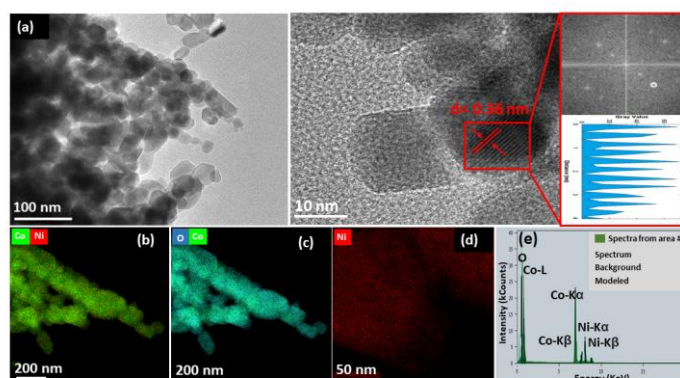


Figure 2. (a) TEM/HRTEM images of pristine NiCo₂O₄ nanostructures and FFT conversion at right side with d-spacing value; (b–d) corresponding elemental mapping of (e) EDS spectra of pristine NiCo₂O₄ nanostructures.

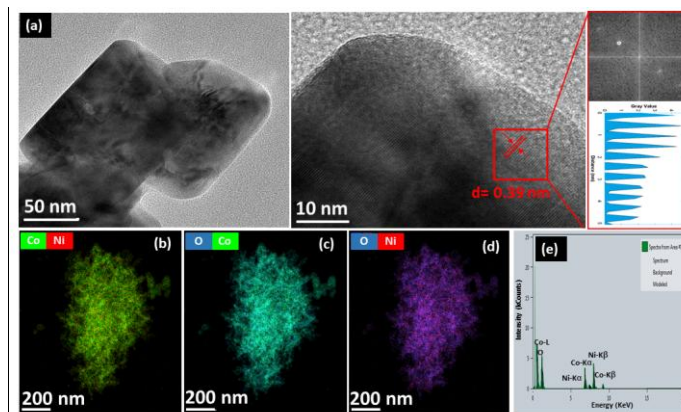


Figure 3. (a) TEM/HRTEM images of NiCo₂O₄ nanostructures prepared with 5 mL of radish white peel extract and FFT with d-spacing value on right-hand side; (b–d) elemental mapping of (e) EDS spectrum of NiCo₂O₄ nanostructures prepared with 5 mL of radish white peel extract.

The presence of green organic reducing, capping, and stabilizing agents in the radish white peel extract have the capability to tailor the surface properties of nanostructured materials [28,42]. Using XPS analysis, we were able to determine the chemical states and surface species of NiCo₂O₄ nanostructures both in the absence and presence of radish white peel extract, as shown in Figure 4. The XPS study has demonstrated a significant role of a wide range of green organic reducing, capping, and stabilizing agents on the surface chemical composition of NiCo₂O₄ nanostructures. To fit the XPS binding energies of each element, a standard carbon binding energy was used. Using pristine NiCo₂O₄ nanostructures as an example, Figure 4a illustrates the Co 2p spectrum, which indicates that there are two types of Co chemical states. According to Figure 5a, the estimated peaks at 779.47 eV and 780.54 eV correspond to the oxidation states of Co³⁺ and Co²⁺, respectively. It is illustrated in Figure 5b how the Ni 2p spectrum can be fitted using Voigt's method. The fitted data consist of two spin orbital doublet peaks, 853.88 eV and 855.60 eV, corresponding to the Ni²⁺ and Ni³⁺ chemical states. It should be noted that despite these limitations, the shakeup peaks have been identified, and the data of Ni 2p fitted to XPS agree reasonably well with the reported peaks [36,44]. Furthermore, Figure 4c displays the O 1s spectrum for pristine NiCo₂O₄ nanostructures in addition to the metallic chemical states. The material surface shows three peaks at 529.69 eV, 531.10 eV, and 532.68 eV, respectively, corresponding to metal–oxygen chemical bonds, oxygen ions, and physisorbed/chemisorbed water. Previous studies [36,44] have detected different oxygenated species on the surface of pristine NiCo₂O₄ nanostructures. The spectrum of O^{1s} at 529.69 eV and 531.10 eV was correlated with the O²⁻ species present on NiCo₂O₄ nanostructures. A similar XPS analysis was conducted on NiCo₂O₄ nanostructures prepared in the presence of 5 mL of radish white peel extract as shown in Figure 4d–f. A large peak was observed in the spectrum of Co 2p associated with oxidation states, such as Co³⁺ and Co²⁺, at 779.57 eV and 781.12 eV, respectively. By contrast, Ni²⁺ and Ni³⁺ were observed at 853.96 eV and 855.61 eV, respectively. Furthermore, three contributions were observed in the O1s spectrum at 529.67 eV, 531.16 eV, and 533.42 eV, corresponding to the metal–oxygen bonds, oxygen ions (O₂), and physisorbed/chemisorbed water on the surface of the material. The XPS study has revealed that green organic reducing, capping, and stabilizing agents from radish white peel extract have a relatively high concentration of oxygen ions (O⁻) and Co³⁺ compared to pristine NiCo₂O₄ nanostructures. These surface properties are highly desirable for a catalytic reaction [36,44]. Furthermore, the green organic reducing, capping, and stabilizing agents have induced a high abundance of Co³⁺/Co²⁺ and Ni²⁺/Ni³⁺ metallic positively charged ions in the surface of NiCo₂O₄ nanostructures. Consequently, these metallic ions have offered a high density of catalytic sites for the favorable electrocatalytic reaction of UA.

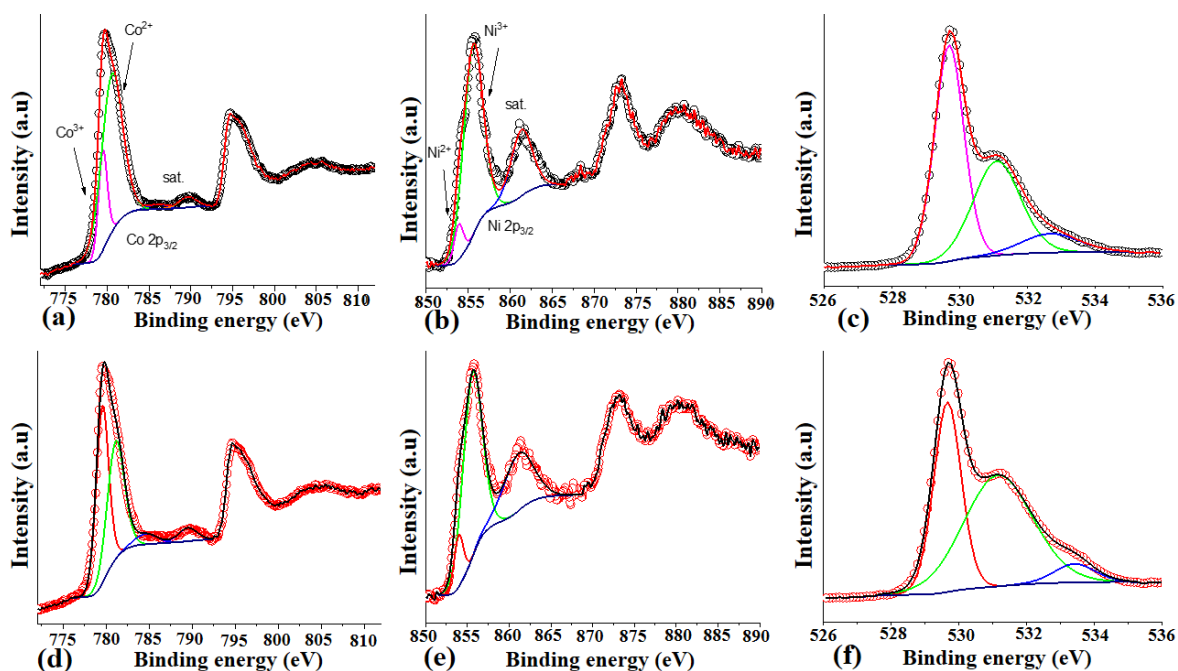
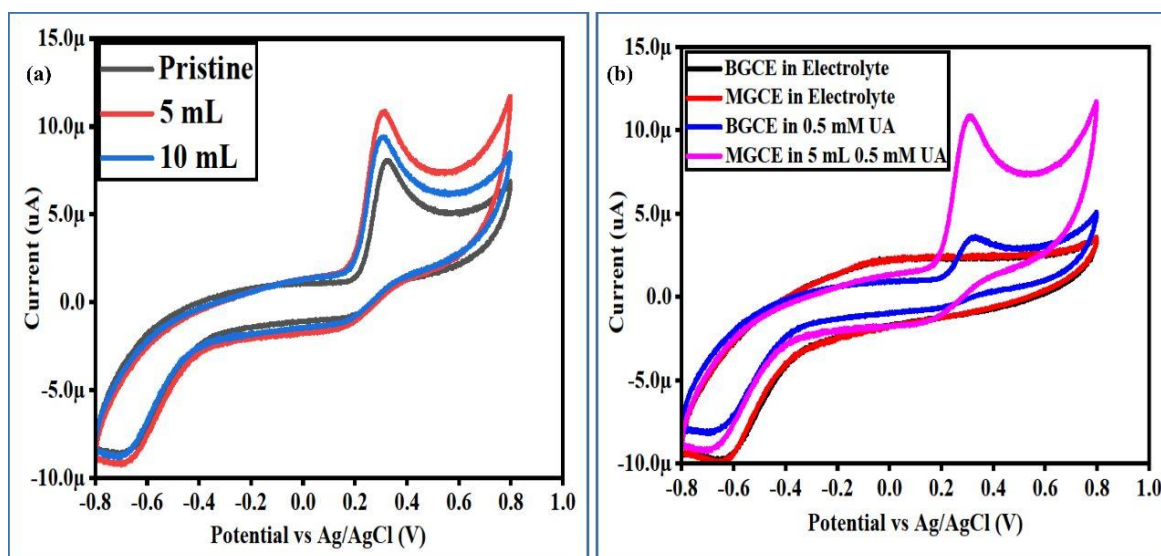


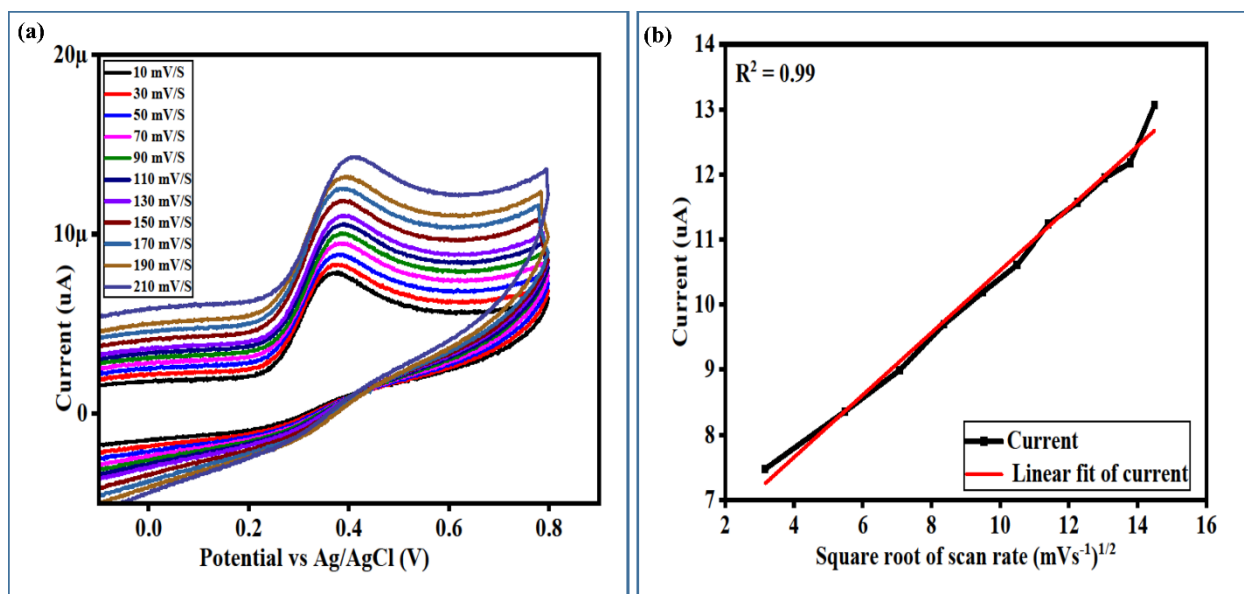
Figure 4. XPS-resolved Co 2p, Ni 2p, O 1s spectra for pristine (a–c) and (d–f) XPS-resolved Co 2p, Ni 2p, O 1s of 5 mL of radish peel extract-assisted NiCo₂O₄ nanostructures.



Figure– 5. (a) Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL and 10 mL of radish white peel extract-assisted NiCo₂O₄ and pristine NiCo₂O₄-modified GCE in the presence of 0.5 mM of UA in 0.1 M PBS pH 7.0. (b) Cyclic voltammograms at 50 mV/s of bare GCE and modified with 5 mL of assisted NiCo₂O₄ in electrolyte and equal in the presence of 0.5 mM UA in 0.1 M PBS pH 7.0.

3.2. Non-Enzymatic Uric Acid (UA) Oxidation on the Surface-Modified NiCo₂O₄ Nanostructures with Radish White Peel Extract

NiCo₂O₄ nanostructures were characterized electrochemically using a three-electrode cell configuration in order to detect UA. Figure 5a illustrates preliminary studies conducted with cyclic voltammetry to identify the most efficient NiCo₂O₄ nanostructures for the oxidation of UA. A CV curve was measured at 50 mV/s using both pristine NiCo₂O₄ nanostructures and NiCo₂O₄ nanostructures, which had been surface-modified with 5 mL and 10 mL of radish white peel extract in the absence or presence of UA. A CV curve, such as that shown in Figure 6a, is representative of electrochemical catalytic signals obtained from pristine and surface-modified NiCo₂O₄ nanostructures placed in 0.5 mM UA in a phosphate buffer solution at pH 7.0. When comparing NiCo₂O₄ nanostructures prepared with 5 mL of radish white peel extract with pristine and surface-modified NiCo₂O₄ nanostructures soaked in 10 mL of radish white peel extract, it is evident that the electrocatalytic properties of these nanostructures are well described when compared to pristine and surface-modified NiCo₂O₄ nanostructures soaked in 10 mL of radish white peel extract. This is due to the enhanced conductivity of the material and the enriched surface sites on the surface. Due to the poor catalytic properties and the electrical conductivity of NiCo₂O₄, the CV curve shows that the peak current is relatively low when UA is oxidized on pristine NiCo₂O₄ nanostructures. However, the electrochemical performance of NiCo₂O₄ nanostructures was strongly dependent on the volume of radish white peel extract, as evidenced by the limited electrochemical signal in Figure 5a for a sample containing 10 mL of radish white peel extract. For the large-scale synthesis of NiCo₂O₄ nanostructures that are highly desirable for electrochemical applications, 5 mL of radish white peel extract appears to provide the best conditions. Moreover, NiCo₂O₄ nanostructures prepared using 5 mL of radish white peel extract and bare glassy carbon electrodes were tested in the presence of 0.5 mM UA and only in the presence of a phosphate buffer solution at pH 7.0, as shown in Figure 6b. UA is believed to cause the signal to originate primarily from NiCo₂O₄ nanostructures; however, the bare glassy carbon electrode, as shown in Figure 5b, did not demonstrate any electrochemical signal for either the electrolyte or analyte. Based on the CV analysis, NiCo₂O₄ nanostructures synthesized with radish white peel extract were only effective for driving UA oxidation in the phosphate buffer solution, thus full non-enzymatic UA sensor characterization was carried out.



Figure– 6. (a) Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL of radish white peel extract-assisted NiCo₂O₄-modified GCE in the presence of 0.5 mM of UA in 0.1 M PBS pH 7.0. (b) Linear plot of peak current against square root of scan rate.

When UA is oxidized on NiCo₂O₄ nanostructures, electrons are transferred from UA to Co³⁺ and Ni³⁺ ions and reduced to Co²⁺ and Ni²⁺. In addition to altering the size and surface properties of NiCo₂O₄ nanostructures, phytochemicals in radish white peel extract enhanced the charge transfer between the electrode and analyte solution. Figure 6a shows the electrode kinetics at various scan rates using CV analysis in a solution containing 0.5 mM UA. It is evident from this example that increasing scan rates linearly increase peak current. This confirms the diffusion-controlled processing of the modified GCE with NiCo₂O₄. As shown in Figure 6b, a linear plot was obtained by plotting the peak current against the square root of the scan rate. The purpose of this was to simplify the understanding of electrode kinetics. NiCo₂O₄ nanostructure-based electrodes have been found to have a high scan rate in recent studies. According to CV analysis, UA oxidation is accompanied by two electron and proton transfers [44–47]. Also, the observed regression coefficient value ($R^2=0.99$) supports the analytical aspects of an enzyme-free UA sensor for precise and accurate quantification of UA. Therefore, surface adsorption and electrochemistry were responsible for controlling the UA oxidation reaction.

Our study examined the effect of pH on the oxidation process of NiCo₂O₄ nanostructures prepared with 5 mL of radish white peel extract. As a result of the pH change of 0.5 mM of UA, CV curves for NiCo₂O₄ nanostructures are illustrated in Figure 7a. We evaluated UA sensor performance at pH 7.0 based on the shape and current of the peak, which were more apparent at this pH level. A pH study indicated that NiCo₂O₄ nanostructures are strongly regulated by the pH of the analyte solution when it comes to their activity. Such aspects have previously been examined in a study [48]. NiCo₂O₄ nanostructures are limited in their ability to function under different pH conditions of analyte solutions. Consequently, the catalytic sites are diminishing, the material is unstable, and the surfaces are etched [49]. As a result of this experiment, the pH of the UA solution was varied between 6.0, 7.0, 8.0, and 9.0. As a result, CV displayed a stable response at pH 7.0, and all electrochemical measurements were made at this pH level. To facilitate interpretation of CV curves, a line plot was also made of the effect of pH on the UA solution. Figure 7b illustrates that pH 7.0 resulted in the highest peak current, which improved charge transfer and increased the NiCo₂O₄ nanostructures' electrochemical activity. UA oxidation occurs when two protons are lost and is suppressed by UA's low pH of 7.0. However, at higher pH levels, NiCo₂O₄ nanostructures are likely to be etched, resulting in poor performance.

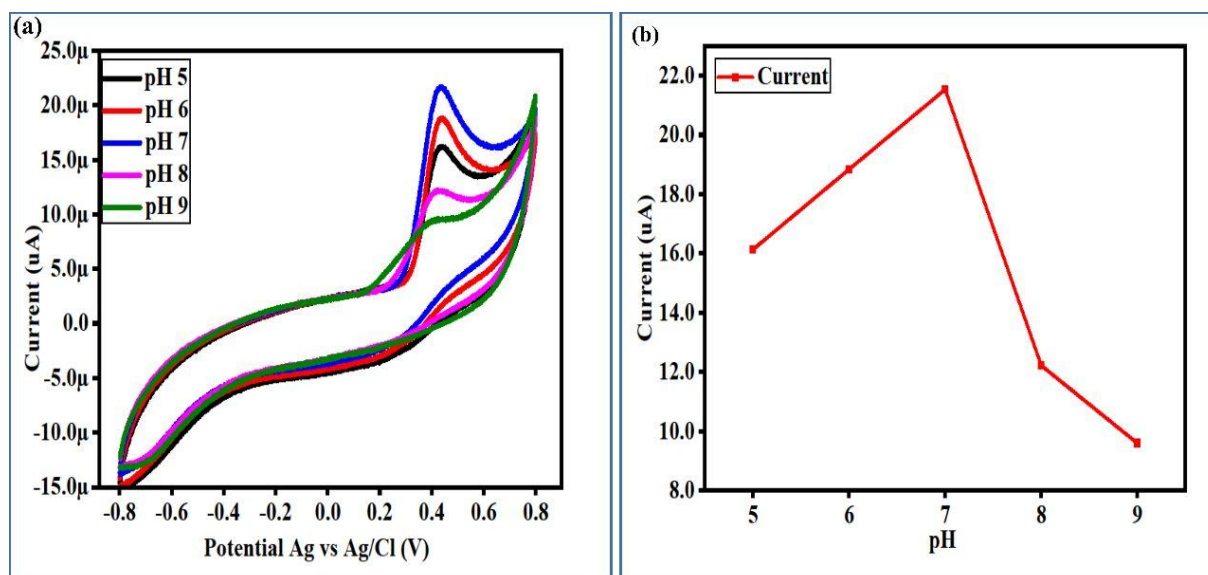


Figure –7. (a) Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL of radish white peel extract-assisted NiCo₂O₄-modified GCE in the presence of different pH values of 0.5 mM of UA in 0.1 M PBS. (b) Linear plot of peak current versus different pH values of 0.5 mM of UA in 0.1 M PBS.

3.3. The Calibration Plots, Stability, Repeatability, and Selectivity Studies of a Newly Developed Non-Enzymatic UA Sensor Based on Surface-Modified NiCo₂O₄ Nanostructures

Analyses of the linear range and limit of detection of UA were conducted using NiCo₂O₄ nanostructures prepared with 5 mL of radish white peel extract. The linear range of a non-enzymatic UA sensor was evaluated by varying electrochemical modes in order to maintain the sensing range of each electrochemical mode. The linear range of UA was first investigated by CV at 50 mV/s in a phosphate buffer solution at pH 7.0 at different concentrations of UA. The linear range of UA was determined to be between 0.1 mM and 8 mM, and the peak current for UA oxidation increased linearly with increasing UA concentration, as shown in Figure 8a. Based on this study, it can be concluded that UA non-enzymatic sensors have demonstrated a wide linear range to date [13,50–56] as well as the low detection limit of 0.005 mM, indicating a high degree of applicability for the monitoring of UA at either low or high concentrations in real samples. In addition, the linear plot shown in Figure 8b was calculated by selecting the oxidation peak current for each UA concentration against the UA concentration in order to determine the accuracy and precision of a newly developed non-enzymatic UA sensor. It appears that UA sensors have the ability to monitor a wide range of UA concentrations from practical samples based on the linear plot of the CV results. On the basis of the methods reported in the literature, a limit of detection (LOD) and a limit of quantification (LOQ) were estimated [56]. In this study, the LOD and LOQ were determined to be 0.005 mM and 0.008 mM, respectively. Table 1 compares the wide linear range of UA detection and the low LOD of the non-enzymatic UA sensors presented with the existing UA biosensors. Following the analysis of the comparisons, it became evident that the proposed method can be of great interest as an alternative method for the detection of UA in real samples, where a wide linear range and a low limit of detection are desired. Additionally, linear sweep voltammetry (LSV) mode was used to estimate the calibration of the newly developed non-enzymatic UA sensor, and Figure 9a illustrates the range of UA detection obtained. Figure 9a illustrates that the proposed UA sensor configuration is capable of detecting UA over a wide linear range from 0.1 mM to 7.0 mM and producing a significant amount of current. When UA concentration increases in LSV measurements, there is a higher current generated, which indicates that the newly developed UA sensor is highly sensitive. Besides the LSV measurements, we also made a linear plot of peak current and UA concentrations (Figure 9b). The linear fitting of LSV curves reveals that the proposed non-enzymatic UA sensor has excellent analytical performance, as indicated by its regression coefficient value of 0.99. Based on full CV curves and half CV curves from LSV, the present UA sensor is capable of detecting a wide linear range of UA with precision and accuracy. Additionally, the linear range for another highly sensitive electrochemical mode of amperometry at 0.3 V was used to determine the linear range of the UA sensor. Figure 10a illustrates this range for various UA concentrations detected. UA concentrations between 0.1 and 6 mM were highly sensitive to the amperometric signal. Figure 10b illustrates a linear plot of the amperometric signal for these different concentrations of UA.

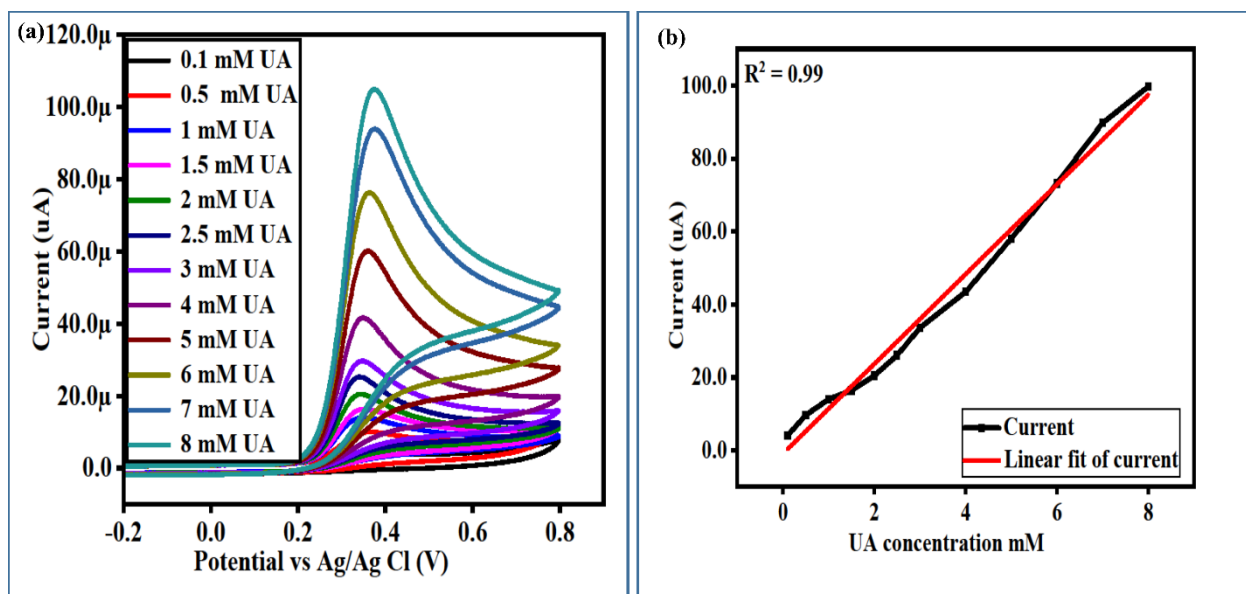
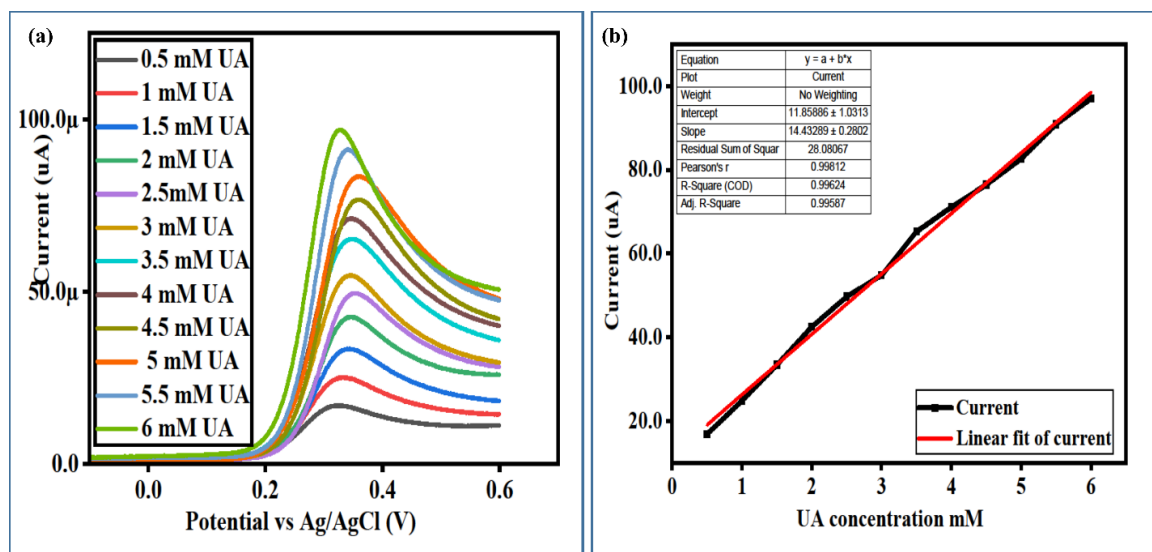


Figure 8. Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL of radish white peel extract-assisted NiCo_2O_4 in the presence of various concentrations of UA in 0.1 M PBS pH 7.0. (b) Linear plot of peak current versus successive increase in UA concentrations.

Table 1. Performance comparison of the enzyme-free sensor based on NiCo_2O_4 nanostructures grown with 5 mL radish (*Raphanus sativus*) extract versus several non-enzymatic UA sensors in the literature.

Sensing Electrode Material	Linear Range (μM)	Detection of Limit (μM)	References
PCN ^a /MWCNT ^b	0.2–20	0.139	[50]
B-MWCNTS ^c	62–250	0.65	[51]
Pd/RGO ^d	6–469.5	1.6	[18]
Au/RGO ^d	8.8–53	1.8	[52]
PtNi@MoS ₂ ^e	0.5–600	0.1	[53]
Cysteic acid	1.0–19	0.36	[54]
Co ₃ O ₄	500–3500	100	[56]
PANI-Pt NPs/GCE	70–1000	1	[59]
MWNTs/MGF	300–1000	0.93	[55]
NiCo ₂ O ₄ (30%)/Nano-ZSM-5	0.9–1000	0.7	[60]
Fe ₂ O ₃ @Au	100–10,000	0.087	[56]
NiCo ₂ O ₄ NPs	100–8000	0.005	This work

^a Porous g-C₃N₄. ^b Multi-walled carbon nanotubes. ^c Boron-doped multi-walled carbon nanotubes. ^d Reduced graphene oxide. ^e PtNi bimetallic nanoparticles-loaded nanosheets.



Figure– 9. (a) Linear sweep voltammetry at a scan rate of 10 mV/s of MGCE with 5 mL of radish white peel extract-assisted NiCo₂O₄ in the presence of various concentrations of UA in 0.1 M PBS pH 7.0. (b) Linear plot of peak current versus successive increase in UA concentrations.

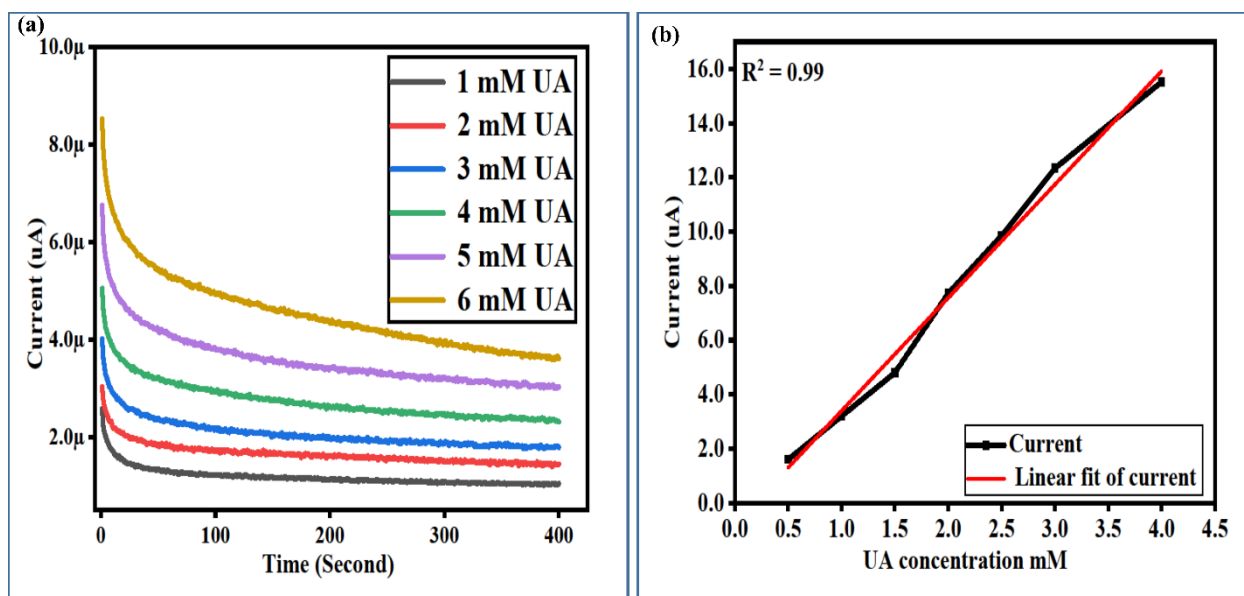
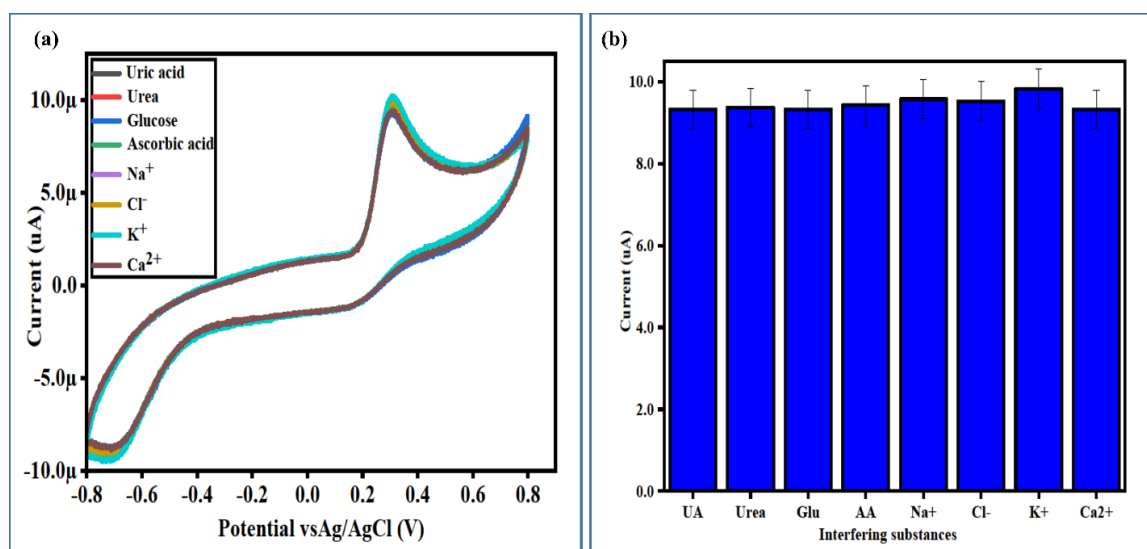


Figure –10. (a) Chronoamperometric response curves measured at an applied potential of 0.3 V of MGCE with 5 mL of radish white peel extract-assisted NiCo₂O₄ in the presence of various concentrations of UA in 0.1 M PBS pH 7.0. (b) Linear plot of peak current versus successive increase in UA concentrations.

A linear fitting of the UA detection resulted in excellent performance with strong analytical features. The results confirm the algorithm's promising performance for the detection of UAs and its application in real-world sample analysis. Due to the high density of catalytic sites, enhanced electrical conductivity, and biomimetic compatibility of nanostructured material with the surface of GCE, UA detection on surface-modified NiCo₂O₄ nanostructures with radish white peel extract presented outstanding linearity and high sensitivity. The SEM, XRD, HRTEM, and XPS measurements demonstrated tailored morphology, excellent crystal quality, a significant amount of surface vacancies, and an abundance of Co(III) and Ni(II) chemical states, which led to the superior performance of NiCo₂O₄ nanostructures prepared with 5 mL of radish white peel extract. In order to evaluate the selectivity of a UA sensor before implementing it in actual sample analysis, we tested the proposed UA sensor in the presence of possible interfering species

during detection of UA in real blood and urine samples. It was determined that the selectivity of the interfering compounds could be monitored by preparing NiCo_2O_4 nanostructures with radish white peel extract containing glucose, ascorbic acid, urea, lactic acid, mannose, sodium ions, chloride ions, potassium ions, and calcium ions, as shown in Figure 11. CV curves were measured following the sequential addition of interfering species to a solution of 0.5 mM UA. Based on Figure 11a, the interfering species had the same concentration as the UA. As a result of the sequential addition of interfering species in the presence of UA, UA was not affected in terms of oxidation peak position, drift in oxidation potential, and peak current, suggesting that the proposed UA sensor configuration has excellent selectivity and is suitable for the detection of UA in biological matrixes. In order to better visualize the variation in UA peak current after the addition of interfering species, a bar graph of the peak current was plotted. The change in peak current could be seen at less than 4%, as shown in Figure 11b. The excellent selectivity of the proposed UA sensor can be attributed to the surface modification of NiCo_2O_4 nanostructures with phytochemicals from radish white peel extract, which enabled it to detect specific electroactive molecules.



Figure– 11. (a) Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL of radish white peel extract-assisted NiCo_2O_4 in the presence of 0.5 mM UA and other competing interfering agents in 0.1 M PBS pH 7.0; (b) bar graph of peak current with addition of interfering species for the illustration of the variation of the peak current.

We examined the repeatability of the modified UA sensor electrode by measuring 20 CV cycles at a scan rate of 50 mV/s in 0.5 mM. It was found that the device could be re-used, as shown in Figure 12a. The long-term stability of UA biosensors is always a challenge, especially for enzymatic biosensors, thus we have designed a non-enzymatic UA sensor with potential application in real analysis. This is evident from the bar graph of peak current after several repeatable CV cycles as shown in Figure 12b. An error of less than 5% indicates the excellent analytical features of the method. A non-enzymatic UA based on surface-modified NiCo_2O_4 nanostructures can be used for long-term applications, since the material does not change surface features under ambient conditions. However, we examined the stability of NiCo_2O_4 nanostructures in 0.5 mM UA solution by measuring the amperometric response over a period of 1000 s. This is depicted in Figure 13a. According to the response time, the present UA sensor did not exhibit any current fluctuation for the selected time. Therefore, it is suitable for long-term applications.

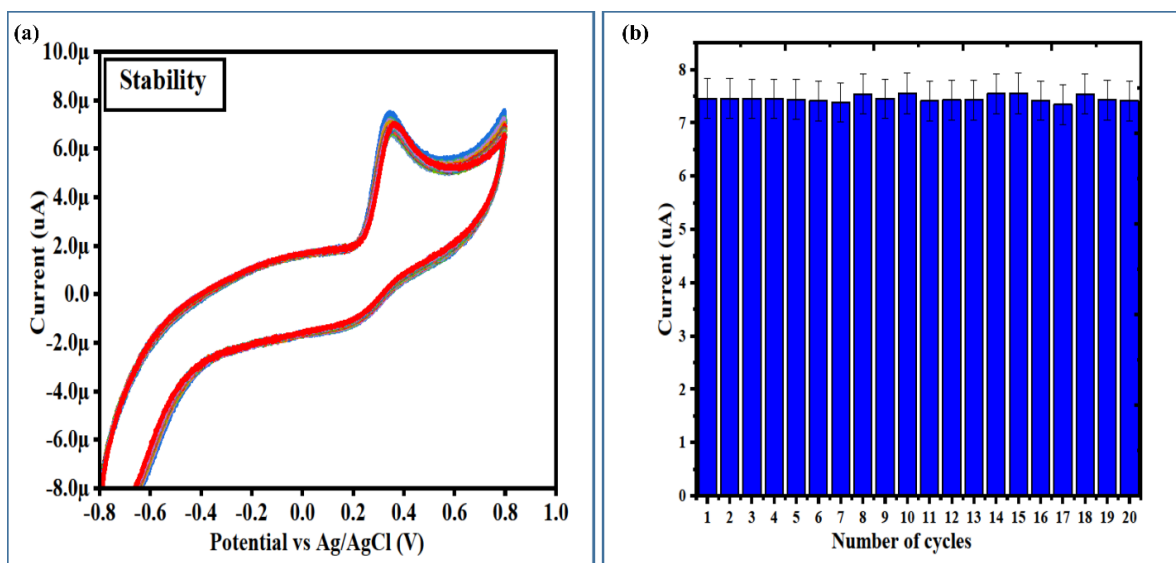


Figure 12. Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL of radish white peel extract-assisted NiCo_2O_4 in the presence of 0.5 mM UA in 0.1 M PBS pH 7.0; (b) bar graph of peak current for the description of change in the peak current with increasing number of CV cycles. Linear plot of peak current versus successive increase in UA concentrations.

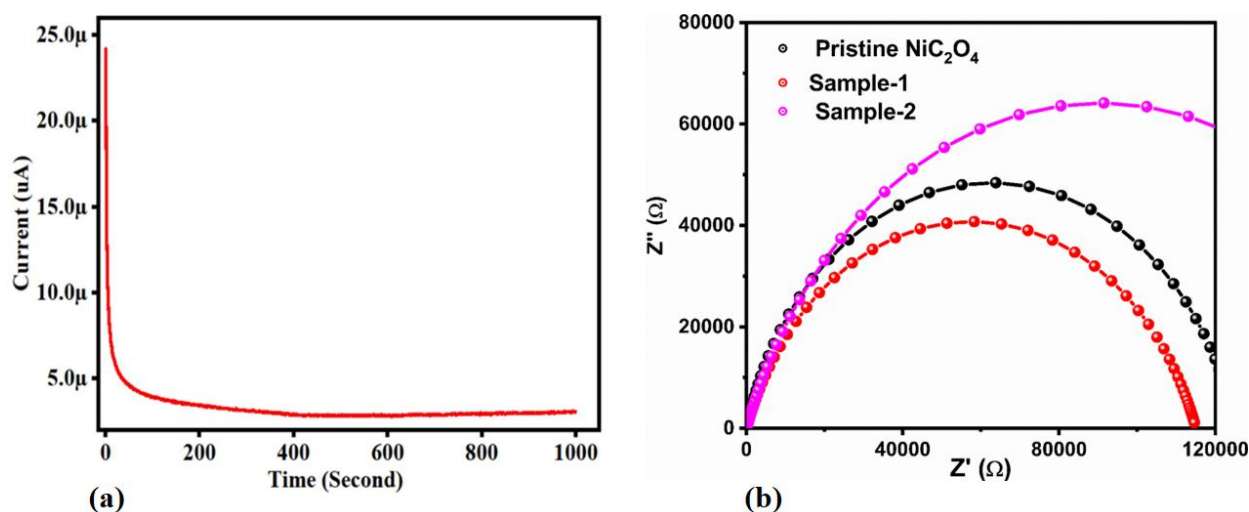


Figure 13. (a) Chronoamperometric response of MGCE with 5 mL of radish white peel extract-assisted NiCo_2O_4 in 0.5 mM prepared in 0.1 M PBS pH 7.0 for the demonstration of stability of modified electrode; (b) EIS Nyquist plots collected for the MGCE with pristine, 5 mL, and 10 mL of radish white peel extract-assisted NiCo_2O_4 in 0.5 mM UA using frequency range of 100 kHz to 1 Hz, amplitude of 10 mV, and biasing potential of 0.6 V.

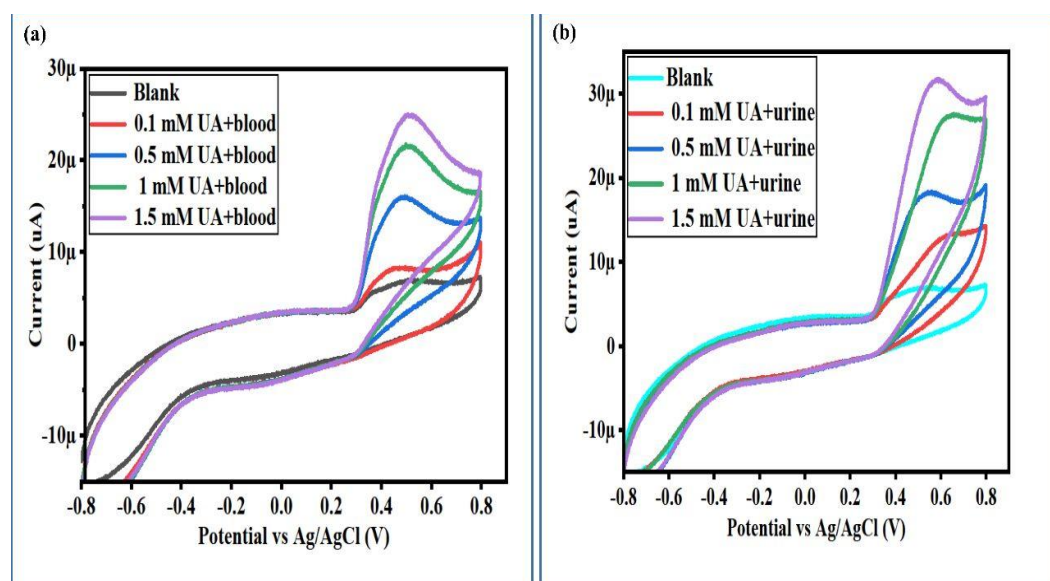


Fig –14. (a) Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL of radish white peel extract assisted NiCo_2O_4 for the quantitation of UA form diluted human blood real samples in 0.1M PBS pH 7.0 and successive addition method, (b) Cyclic voltammograms at a scan rate of 50 mV/s of MGCE with 5 mL of radish white peel extract assisted NiCo_2O_4 for the quantitation of UA form diluted human urine real samples in 0.1M PBS pH 7.0 and successive addition method.

Our results in terms of wide linear range, low limit of detection, excellent selectivity, stability, and repeatability confirmed the superior performance compared to other UA sensors/biosensors reported in the existing literature, as shown in Table 1. To support the electrochemical performance of the prepared NiCo_2O_4 nanostructures, electrochemical impedance spectroscopy (EIS) was performed using a sweeping frequency range of 100 kHz to 1 Hz, amplitude of 10 mV and biasing potential of 0.6 V. The Nyquist plots were measured for the three samples of NiCo_2O_4 nanostructures, including pristine sample 1 and sample 2 in 0.5mM UA, and the EIS data were fitted with Z-view software as illustrated in Figure 13b. The intercept of the semicircle of Nyquist plots at high frequency represents electrolyte resistance. The arc of the Nyquist plots indicates the charge transport between the working electrode based on NiCo_2O_4 nanostructures and the 0.5mM analyte solution [60]. The estimated values of charge-transfer R_{ct} for pristine NiCo_2O_4 nanostructures, sample 1, and sample 2 in the presence of analyte were as 125,100 Ohm, 114970 Ohm, and 181,270 Ohm, respectively. The EIS study has verified that sample 1 of NiCo_2O_4 nanostructures prepared with 5 mL of radish white peel extract has more favorable charge transport over the pristine and sample 2-based NiCo_2O_4 nanostructures; hence, we observed better electrochemical measurements of sample 1 toward the quantification of a sensitive UA signal.

3.4. Human Blood Sample Analytical Applications of Proposed Non-Enzymatic UA Sensor-Based NiCo_2O_4 Nanostructures

The non-enzymatic UA sensor configuration presented in Figure 14a,b has been evaluated on real human blood samples. A healthy volunteer and a high UA patient provided blood samples with their own consent. The samples were diluted 30 times with 0.1 M phosphate buffer solution of pH 7.0 and used directly during the setup of three electrode cells for electrochemical quantification of UA. UA non-enzymatic sensor performance confirms its potential applicability and reliability for the quantification of UA from biological fluids, and even food products with high probability, as shown in Table 2. A percent relative standard deviation RSD (%) was calculated from the sum of (standard deviation/mean of quantified UA concentration data using three repeated experiments for UA detection) \times 100%.

Table 2. Real sample analysis of UA from various blood samples (Blood 1 = healthy blood sample; Blood 2 = high-level UA patient).

Sample	Added (mM)	Found (mM)	%Recovery	% RSD
Blood 1	-	0.1	-	-
-	0.5	0.612 ± 0.002	101.66	0.52
-	1	1.123 ± 0.0023	101.81	0.53
-	2	2.084 ± 0.0017	99	0.49
-	2.5	2.621 ± 0.0013	100.77	0.54
Blood 2	-	1.00	-	-
-	1.5	2.533 ± 0.0022	101.2	0.48
-	2	3.082 ± 0.0019	102.66	0.56
-	2.5	3.514 ± 0.0024	100.28	0.50
-	3	4.063 ± 0.0018	101.5	0.53

4. Conclusions

An easy and rapid method has been developed for quantifying UA in human blood and urine samples by using surface-modified NiCo₂O₄ nanostructures. It has been combined with phytochemicals derived from radish white peel. It was determined that a volume of 5 mL of radish white peel extract was optimal for the large-scale synthesis of NiCo₂O₄ nanostructures. The CV exhibited a linear range from 0.1 mM to 8 mM, the LSV showed 0.1 mM to 7 mM, and the amperometric signal for the UA sensor showed a linear range from 0.1 mM to 4 mM. We found that the LOD and LOQ of the present non-enzymatic UA sensor were 0.005 mM and 0.008 mM, respectively. Furthermore, the present UA sensor was evaluated in terms of its selectivity, stability, repeatability, and sensitivity. Consequently, a wide linear range and a low limit of detection were achieved. Several factors contribute to the sensor's performance, including large surface vacancies, abundant chemical states of Co(III), Ni(II), tailored surface morphology, fast charge-transfer rate, and outstanding crystal quality. It has been demonstrated that there is a satisfactory level of detection of UA in human blood samples (healthy and UA patients).

Author Contributions: A.G.S. performed material synthesis and partial electrochemical measurements; A.T. performed XRD analysis and measurement; B.W. performed the real sample analysis; A.S.C. performed the partial electrochemical measurement and analyzed the obtained results; T.P. performed the partial supervisions and preview the obtained results; A.N. performed validation of results and proofread the paper; E.A.D. performed SEM analysis; L.M.A.S. performed EIS study; M.P. performed HRTEM analysis; A.H.I. performed overall review of the obtained results; K.L. performed XPS and HRTEM measurement; B.V. performed XPS analysis and proofread the structural results; Z.H.I. performed main supervision and wrote the first draft of manuscript. All authors have read and agreed to the published version of the manuscript.

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