NiOx electrochemical sensor fabricated via electrodeposition and spin-coating

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Abstract

NiOx thin films were prepared on an Au substrate using the electrodeposition (ED), spin-coating (SP), and ED after SP (SP/ED) techniques to realize their application as an electrochemical sensor for the selective detection of trace substances. Results indicated that the electrodeposited films had nanoparticles formed as coarse-grain morphology, and the spin-coated films had a uniform layer with ˜60 nm thickness. The thin film prepared by the SP/ED technique showed the highest electrochemical activity, and it was used to record a linear sweep voltammogram to measure the target substance, MSG and glucose, from low concentrations (2 nM) to high concentrations (200 µM). Within the range of concentrations, high R2 values of [?]0.99 were observed for both target substances, confirming that the SP/ED thin films can be used as an electrochemical sensor with high reliability.

NiO_x electrochemical sensor fabricated via electrodeposition and spin-coating

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Introduction : Electrochemical sensors are widely used in various industries, including biotechnology, medicine, food, environment, and agriculture owing to their low detection threshold and fast detection [1]. Depending on signals used for detection (i.e., current, voltage, and impedance), electrochemical sensors are divided into different types [2]. The optimal detection technique can be applied by identifying the driving method and signal type, according to the type and concentration of the target substance. Among various analytical techniques that utilize electrochemical sensors, voltammetry is widely used in biotechnology and environment, where trace substance is to be detected [3].

Electrochemical sensors are advantageous due to their handiness, low cost, easiness to use, fast operation, and reliability of measurements, making them useful for real-time quantitative analysis. Recently, the applications of electrochemical biosensors have been extended to various industry; they are used to quantify the

amount of food additives that affect human body. Since the safety of food additives such as monosodium glutamate (MSG; generally, L-glutamate) or sugars (typical glucose) has been in question, the importance of quantitative detection technique, for the post-processing analysis of such additive and their impact on human body after ingestion, has been acknowledged widely [4]. The most common approach for real-time quantitative analysis of glutamate or glucose is the enzyme-based electrochemical detection. Although enzyme-based electrochemical sensors exhibit high sensitivity, excellent selectivity, and low detection thresholds, expensive enzymes, complex enzyme immobilization procedures, limited stability and reproducibility, and indirect quantitative measurement of analytes by enzymes limit their application. Thus, non-enzymatic electrochemical sensor systems that detect a target substance through direct electrocatalytic oxidation of the materials having high electrochemical catalytic activity are actively investigated [5, 6]. The non-enzymatic techniques using such transition metal oxides are attracting considerable attention because of their low cost, high stability, facile reaction, wide detection range, and low detection threshold. Particularly, NiO_x are widely used because of their high electrochemical catalytic activity, excellent chemical stability, and low cost. NiO_x can be deposited on an electrode, in various forms or structures, such as thin nanofilms, nanoparticles, nanosheets, nanoflakes, or nanospheres using various techniques, such as low vacuum evaporation (LVE), electrodeposition (ED), sol–gel treatment, spin-coating (SP), ultrasonic spray deposition, hydrothermal method, and chemical bath deposition [7, 8].

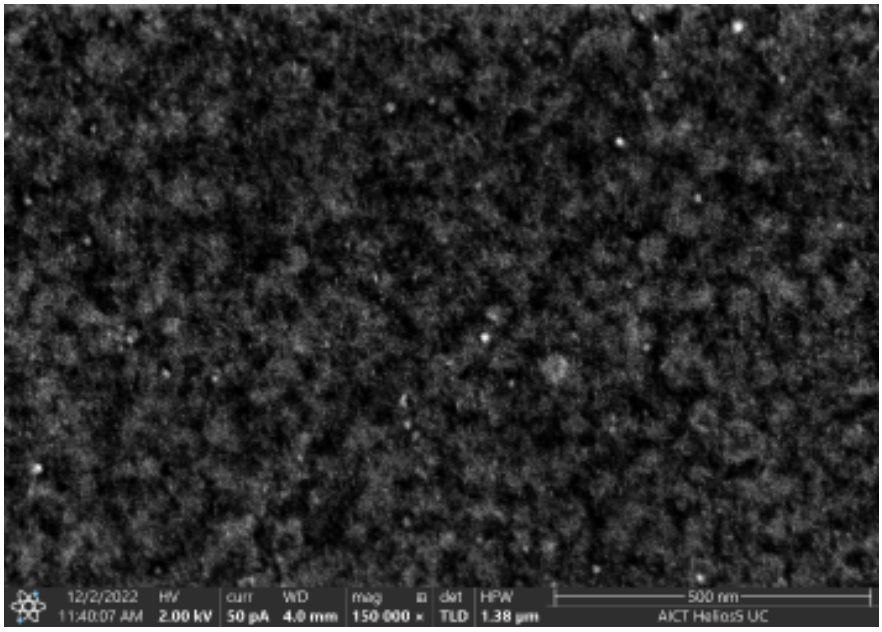
Herein, NiO_x were applied to an electrochemical sensor system by modifying the electrode surface through ED and SP techniques. By adopting SP and ED techniques in a sequence, a NiO_xthin film was formed, and NiO_x nanoparticles were further introduced, yielding an electrode with improved electrochemical activity. The resulting electrode was examined for its performance as an electrochemical sensor for detecting trace MSG and glucose.

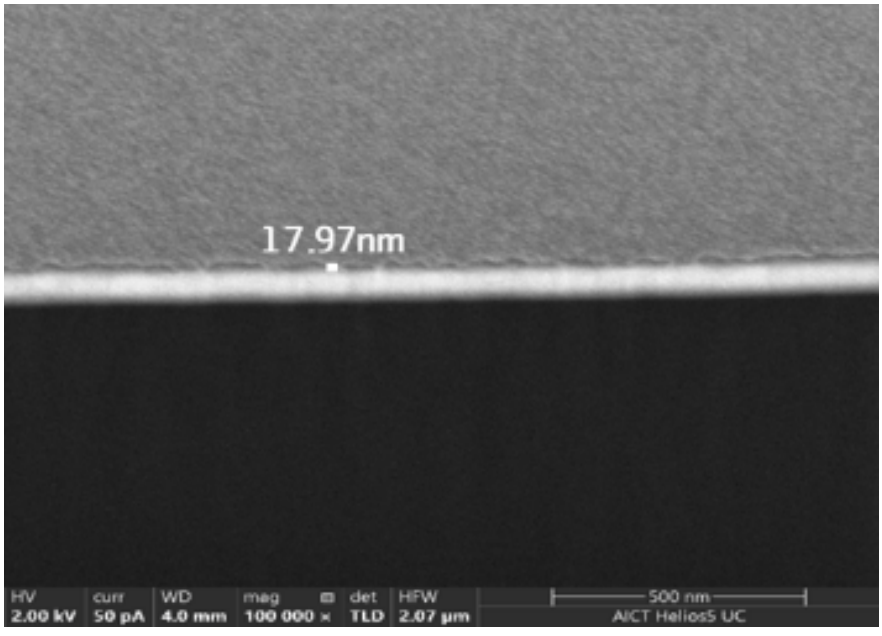
Experimental methods: The NiO_x thin films were prepared on an Au wafer using three techniques: 1) Electrodeposition (ED); 2) Spin-coating (SP); and 3) ED after SP (SP/ED) techniques. The Au wafer is a commercial substrate with 100 nm of Au deposited on a Si wafer. Before use, the Au wafer was treated with piranha solution (sulfuric acid: hydrogen peroxide, 3:1) to remove any organics or impurities. To electrodeposit NiO_x, a pretreated Au wafer, Ag/AgCl electrode, and Pt coiled-wire was used as the working, reference, and counter electrodes. A precursor solution for the ED was prepared by dissolving 0.5 mM nickel (II) nitrate hexahydrate in 0.1 M phosphate buffer solution with pH 7.0. NiO_x was plated on the substrate by applying a constant potential of -1.1 V (vs. Ag/AgCl electrode) for 1 h, and the change in current was observed over time. The spin-coated NiO_x thin film was prepared through a combustion process [9]. A solution was prepared by dissolving 2.7 g nickel (II) nitrate hexahydrate in 10 ml 2-methoxyethanol, with further addition of 200 µL acetylacetone. The substrate pretreatment was performed at 40°C with an ozone generator to increase the affinity between the spin coating solution and the substrate. SP was performed under conditions of acceleration time of 5 sec, rotation speed of 3000 rpm, and rotation time of 45 sec. Then, the substrate was heat treated at 250°C for 45 min to form an oxide film.

To characterize the electrochemical performance of the NiO_x modified electrodes and their detecting performance of MSG and glucose, electrochemical experiments were performed in a three-electrode system using a potentiostat (Metrohm Autolab). The NiO_x electrode, Ag/AgCl electrode, and Pt coiled-wire were used as the working, reference, and counter electrodes, respectively. The electrochemical oxidation–reduction reaction of NiO_x was demonstrated by cyclic voltammetry (CV; 0.15–0.55 V) in a 0.5 M NaOH solution. To validate the electrochemical sensing of MSG and glucose, linear sweep voltammetry (LSV; 0.2–0.6 V) was performed to record current change at different concentrations.

Experimental results: Fig. 1 illustrates the surface and cross-sectional structure of the thin film observed by FIB-SEM. NiO_x was well prepared on the gold substrate by ED and nanoparticles exhibit coarse-grain morphology (Fig. 1*a*). The nanoparticles were uniformly electrodeposited on the electrode surface (˜18 nm thick; Fig. 1*a*). The spin-coated film had NiO_x agglomerates dispersed throughout a smooth surface, and it formed a ˜60 nm thick layer, which is thicker than the electrodeposited film (Fig. 1*b*). The SP/ED thin films generated an electrodeposited nanoparticle layer (˜67 nm thick), which has a coarse-grain morphology

on a spin-coated NiO_x layer (Fig. 1*c*).





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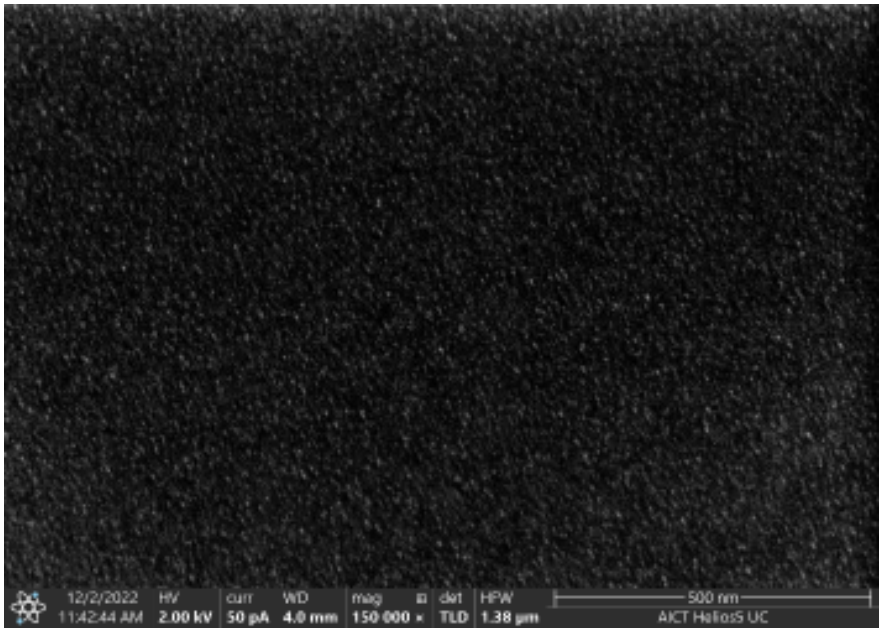

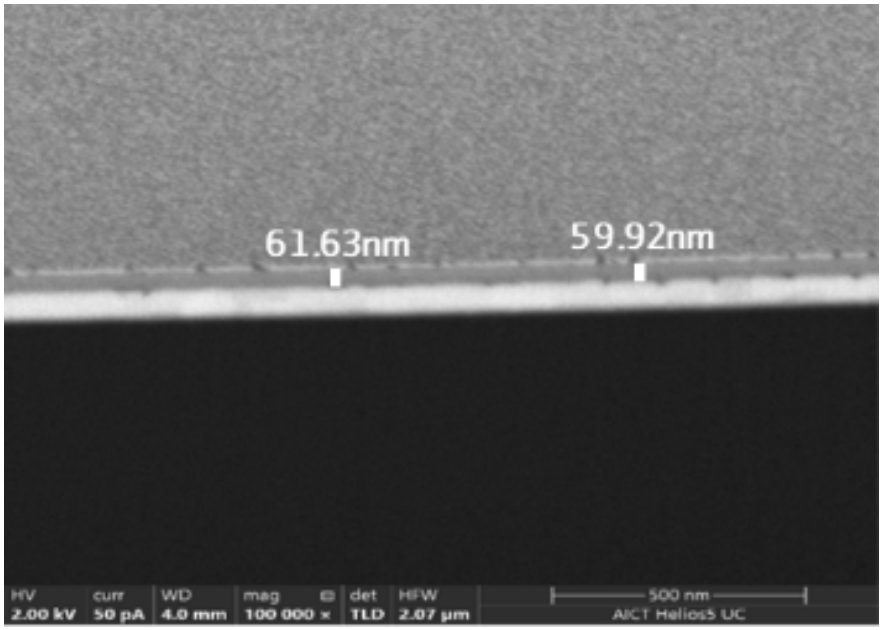

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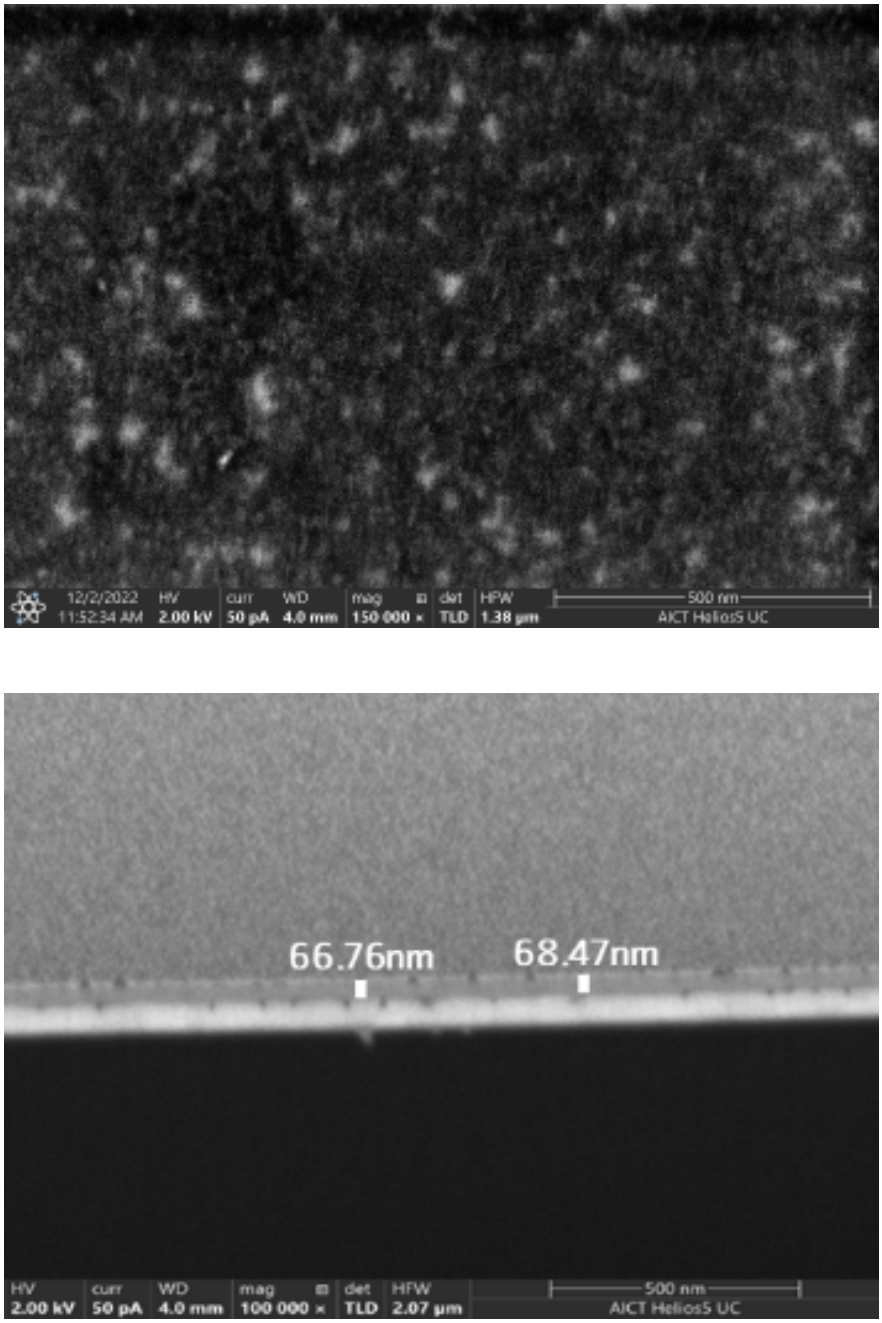


c

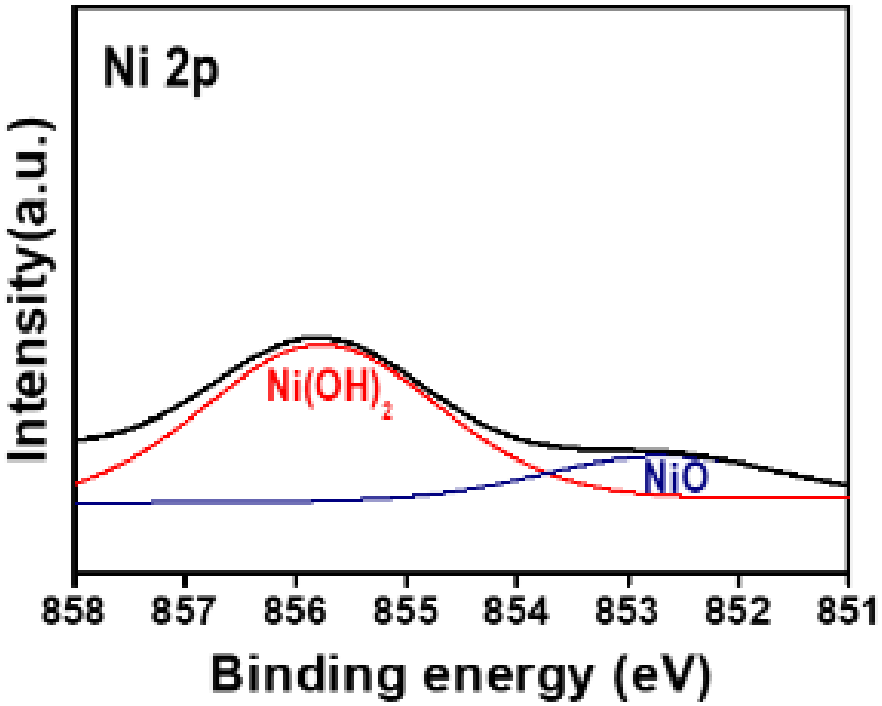
Fig. 1 *SEM images of the surface (left column) and cross-section (right column) of Au wafer electrodes modified with NiO_x according to fabrication methods*

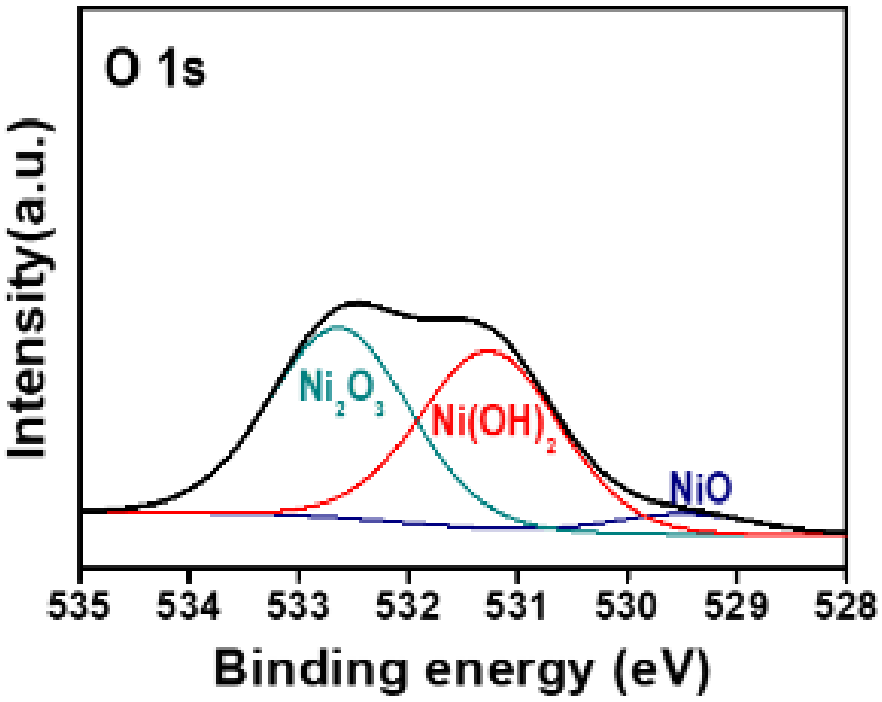
a by electrodeposition (ED)

b by spin-coating (SP)

c by spin-coating/electrodeposition (SP/ED)

X-ray photospectroscopy (XPS) was performed to analyze the elemental and chemical characteristics of the NiO_x thin films according to surface modification methods (Fig. 2). The Ni (2p) of the cleaned nickel oxide foam can be deconvoluted into two peaks at 856.12 eV and 854.21 eV, corresponding to $Ni(OH)_2$ and NiO (Fig. 2*a–c* left column). The O (1s) spectrum of NiO_xfilms showed a fit to three curve peaks, composed of Ni_2O_3, $Ni(OH)_2$ and NiO at 532.68 eV, 531.24 eV and 529.48 eV, respectively (Fig. 2*a–c*right column) [10, 11]. A large amount of NiO_x was identified on the surface of the thin films, mainly composed of $Ni(OH)_2$ and NiO in the Ni (2p) and O (1s) spectra. In particular, it was observed that the intensity of obvious peaks corresponding to $Ni(OH)_2$ and NiO were the highest in the NiO_x thin film fabricated by the SP/ED technique, which indicates that the electrode surface was formed with improved electrochemical catalytic activity.





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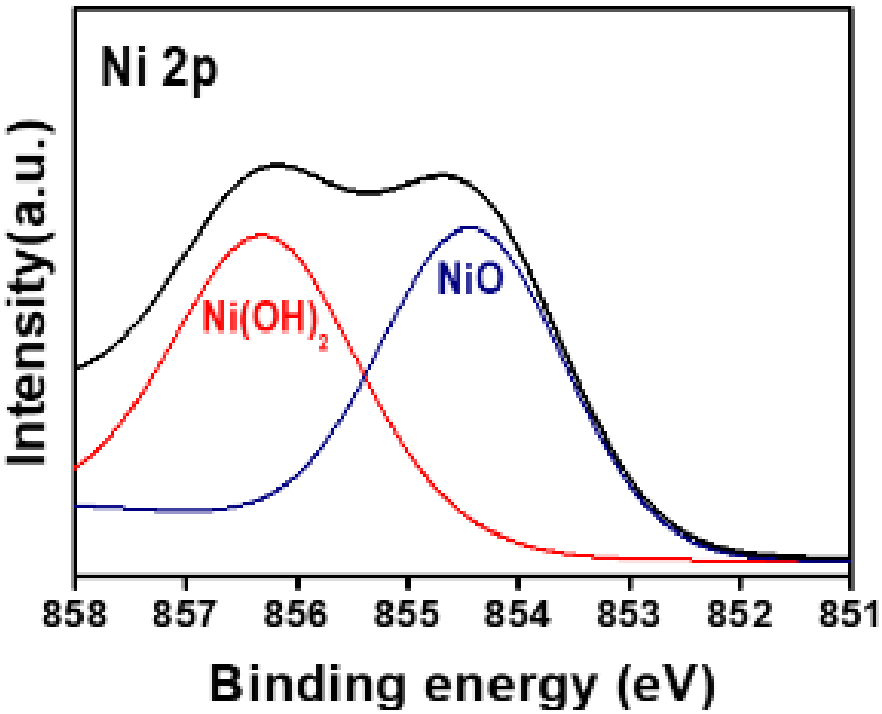

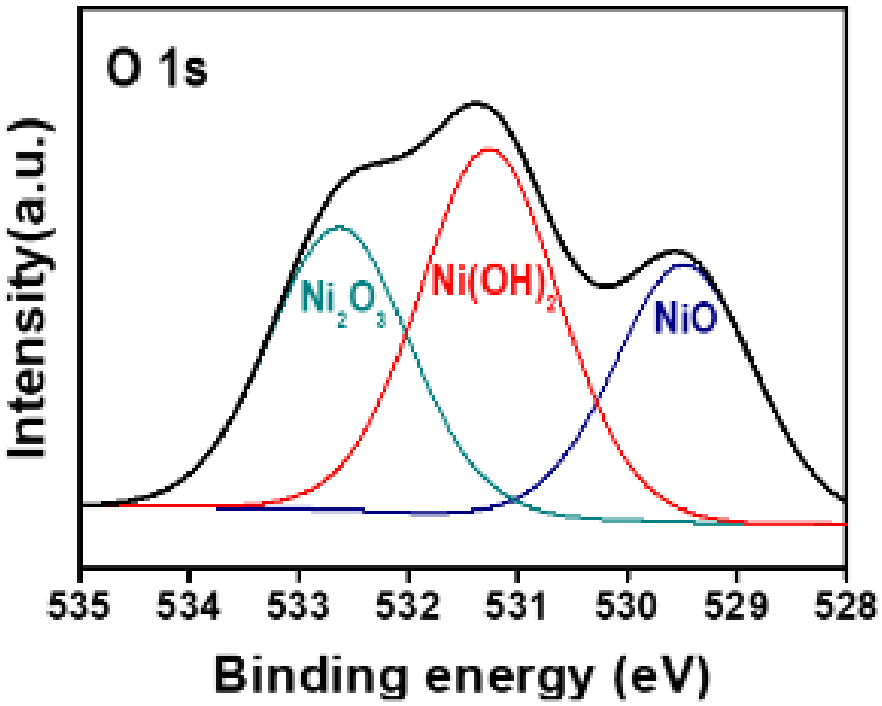

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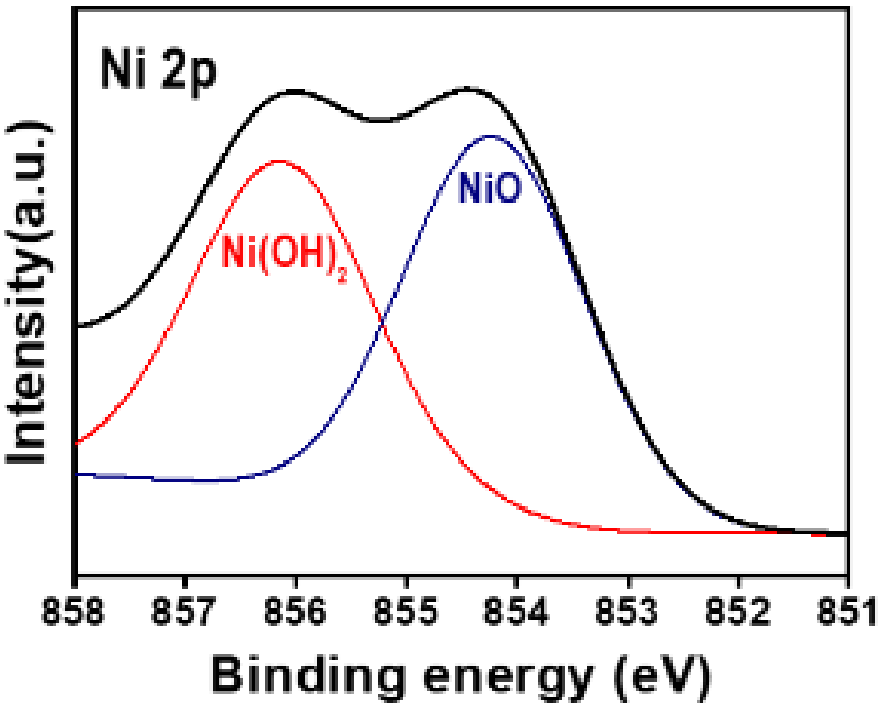

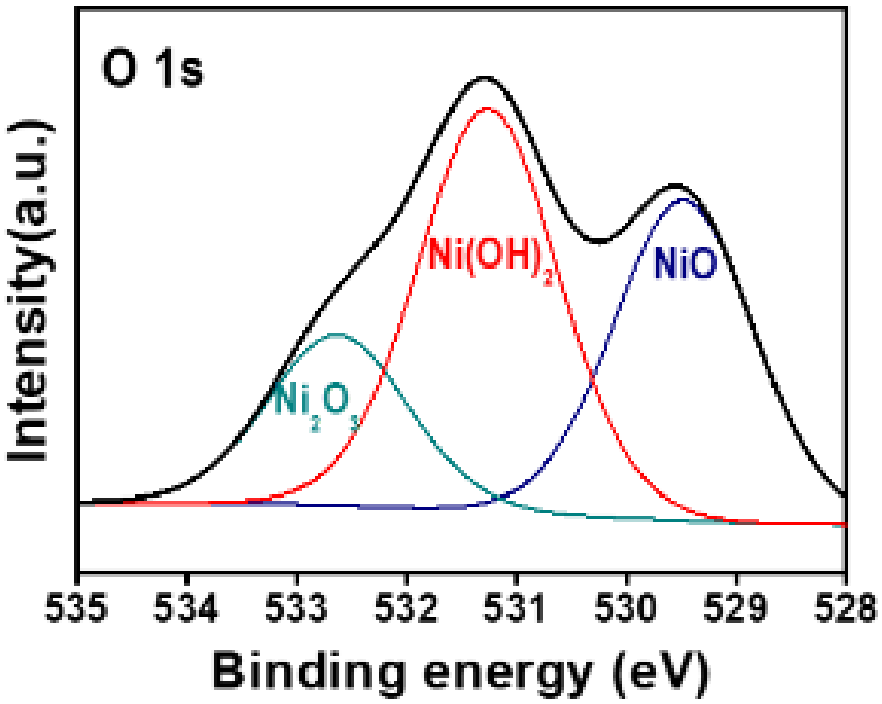

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Fig. 2 *XPS spectra of the Ni (2p) (left column) and O (1s) (right column) of the NiO_x-modified Au wafer electrodes by fabrication methods of*

a electrodeposition (ED)

b spin-coating (SP)

c spin-coating/electrodeposition (SP/ED)

To determine the electrochemical properties of NiO_x thin films, a CV was recorded at a scan rate of 0.1 V s^{-1}(Fig. 3). The redox peaks of NiO_x for the oxidation–reduction reaction (NiO or $Ni(OH)_2$ / NiOOH due to Ni(II) / Ni(III) conversion) were well identified for the all different electrodes. The oxidation/reduction potentials of the NiO_x thin films prepared by ED technique were 0.38V and 0.32V, and the oxidation/reduction peak current densities were 0.57 × 10^{-4} A cm^{-2} and -0.45 x 10^{-4} A cm^{-2}, respectively. The NiO_x thin films fabricated by SP technique showed oxidation/reduction potentials at 0.4 V and 0.33 V, and the oxidation/reduction peak current densities were 0.88 x 10^{-4} A cm^{-2} and -0.72 x 10^{-4} A cm^{-2}, respectively. The spin-coated/electrodeposited (SP/ED) electrode with the thickest NiO_x thin film showed oxidation/reduction potentials at 0.41 and 0.33 V, and the oxidation/reduction peak current densities were the highest, 1.25 x 10^{-4} A cm^{-2} and -1.08 x 10^{-4} A cm^{-2}. As the effective surface area of the NiO_x on the modified electrode increases (Fig. 1), the oxidation/reduction peak current, and thus capacitance, increased. The electrochemical activity and electrode performance were improved by modifying the surface with NiO_x films, nanofilm and nanoparticles, on the Au wafer electrode by SP/ED technique. Thus, the modified electrode was useful as an electrochemical sensor.

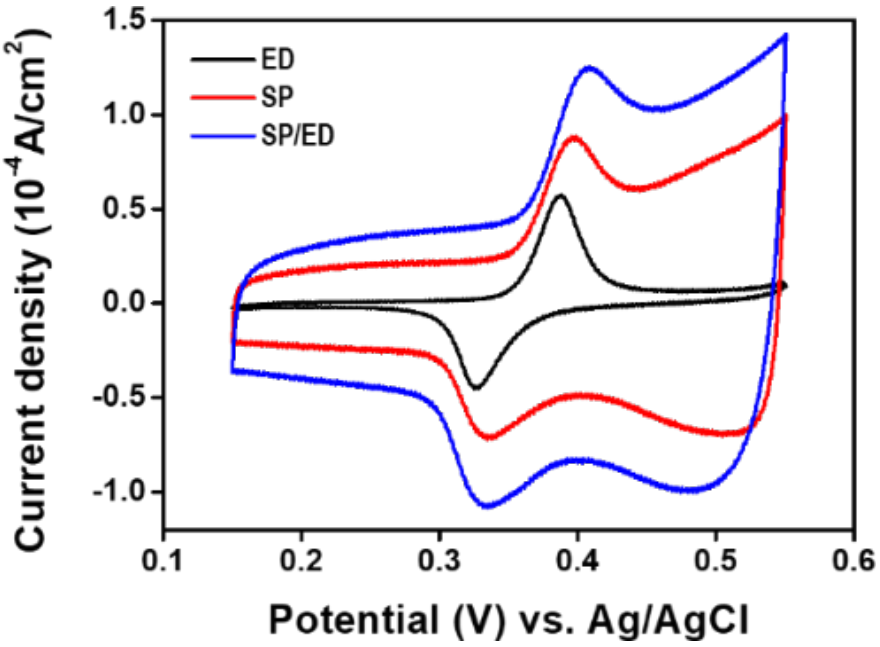
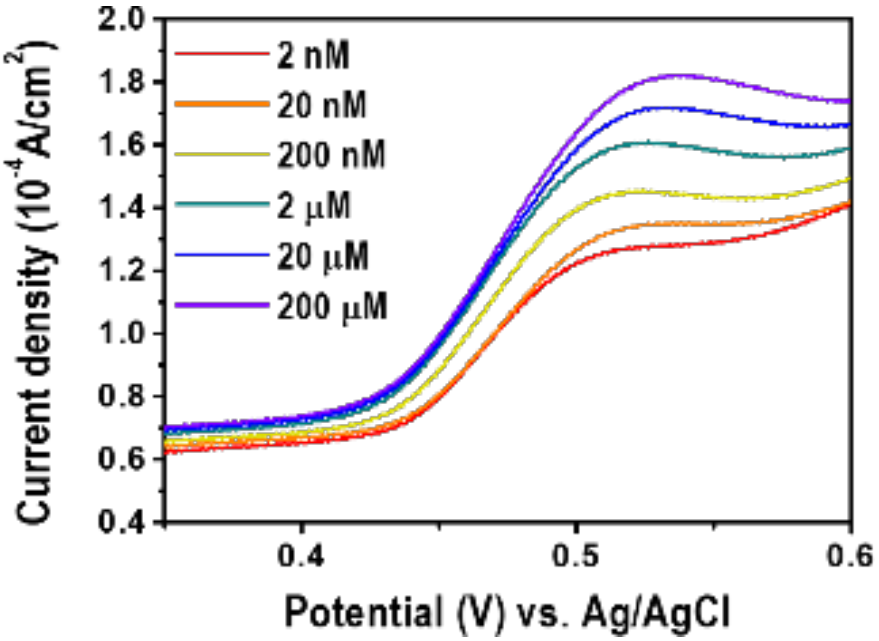
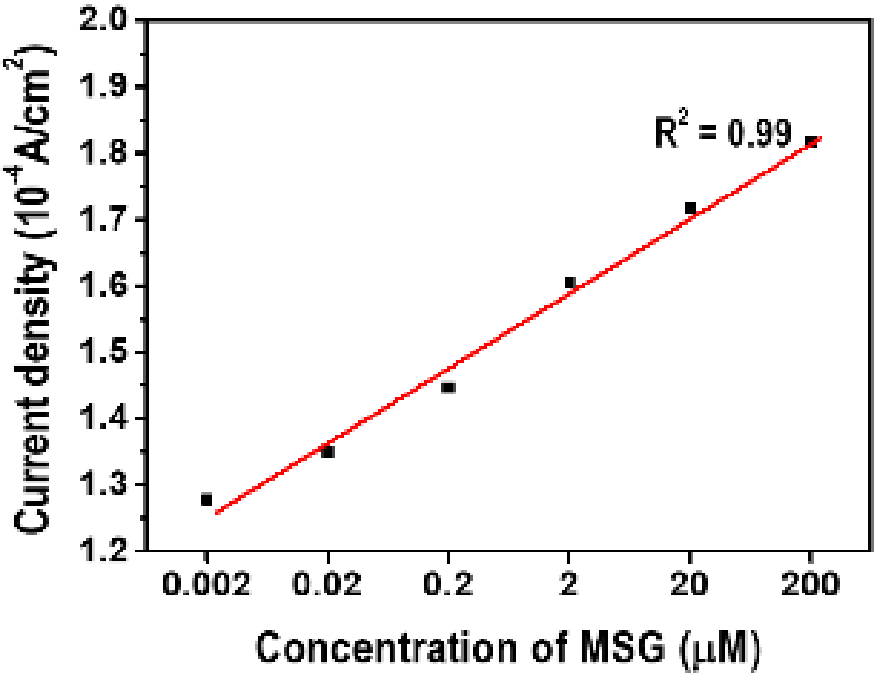


Fig. 3 *CVs of Au wafer electrodes modified with NiOx by electrodeposition (ED), spin-coating (SP), and spin-coating/electrodeposition (SP/ED) in 0.5 M NaOH (0.1 V s^{-1}scan rate)*

To determine application potential the thin film modified with NiO_x as a biosensor electrode, a LSV was performed at different concentrations of the target substances. All thin films showed a positive shift in oxidation peak potential as the concentration of the target substance was increased, but the current at the oxidation peak potential was increased. It means that when the concentration of the target substance increases, the detection sensitivity also increases, and the substance can be detected stably and sensitively. In this study, the NiO_x modified electrode prepared by SP/ED was finally selected as an electrochemical biosensor electrode. The LSV for the electrode, recorded at different concentrations, is shown in Fig. 4 (right column). From the results, a calibration curve for different concentrations (2 nM–200 μM) of the target substances was obtained with current values at 0.53 V, the average peak potential value. The R^2 value of [?]0.99 indicated high reliability. Therefore, the electrode modified with NiO_x via SP/ED is suitable for an electrochemical sensor for detecting trace MSG and glucose of different concentrations.





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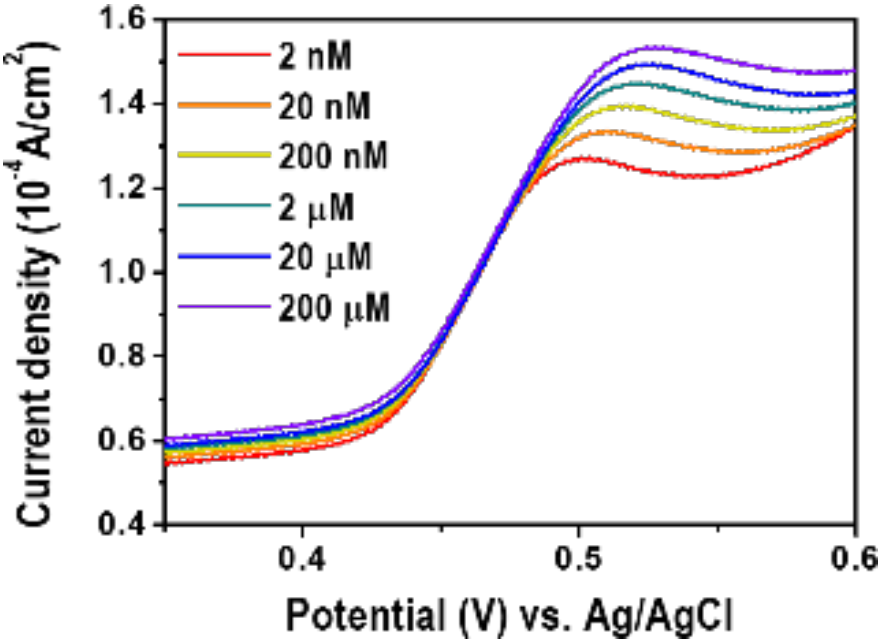

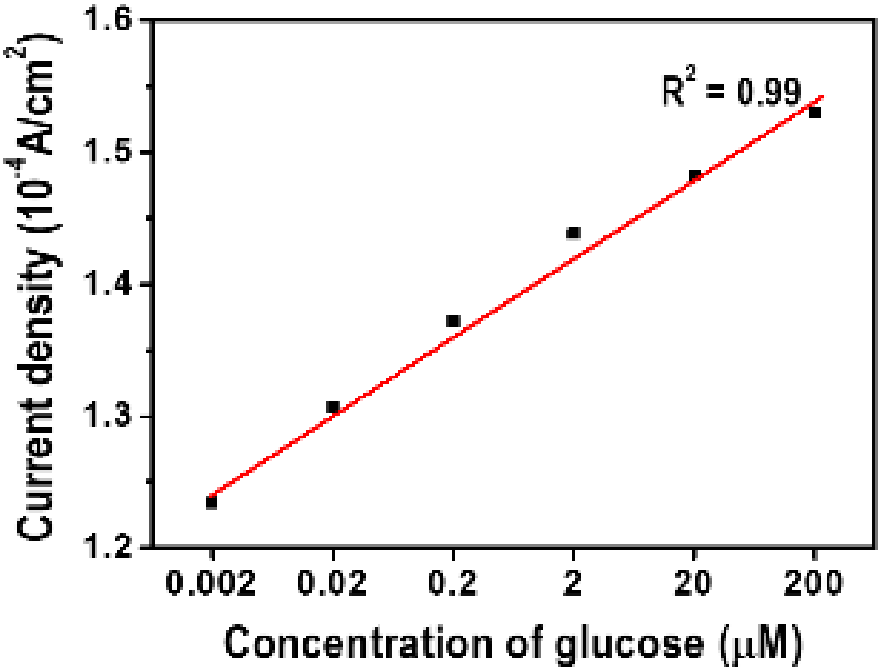

b

Fig. 4 *LSV curves (left column) of the NiO_x(SP/ED)-Au wafer electrode in 0.1 M NaOH containing different concentrations of targets and calibration curves (right column) of the oxidation peak current at 0.53 V versus concentrations of targets*

a MSG

b glucose

Conclusion: To examine whether the NiO_x film can be applied as an electrochemical sensor for selectively detecting trace substance, the prepared thin films' surfaces were examined via FIB-SEM and XPS. FIB-SEM analysis showed that an ˜18 nm thick nanoparticle layer was formed when the film was fabricated via ED, a uniform thin film (˜60 nm thick) was formed via SP, and films with highest thickness (˜70 nm) was obtained via SP/ED, in which nanoparticles are formed on a uniform spin-coated nanofilm. The results of XPS analysis showed that various forms of NiO_x were present, including NiO, Ni_2O_3, and $Ni(OH)_2$, in the thin films fabricated by ED and SP techniques. NiO_xcontent (the amount of NiO) increased when films were fabricated via SP. The oxidation–reduction behavior of the electrode modified with NiO_x was investigated in a three-electrode system to understand the electrochemical properties. The highest electrochemical activity of the NiO_x electrode was observed for films prepared via SP/ED, thus validating its performance as a sensor. The target substances, MSG and glucose, were detected at different concentrations, and a calibration curve was plotted in the range 2 nM–200 μM with the R^2 value of [?]0.99, indicating high reliability.

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