



Ruthenium oxide modified nickel electrode for ascorbic acid detection



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HIGHLIGHTS

- A non-mediated sensor, RuO_x/Ni, was prepared to sense ascorbic acid.
- The littered nano-RuO_x electrode presents the highest sensitivity.
- The ascorbic acid proceeds an irreversible electrochemical reaction.
- The RuO_x/Ni sensor showed good selectivity among eight interfering reagents.
- After 38 days of intermittent testing, the sensitivity remained almost constant.

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ABSTRACT

Electrodes of ruthenium oxide modified nickel were prepared by a thermal decomposition method. The stoichiometry of the modifier, RuO_x, was quantitatively determined to be a meta-stable phase, RuO₅. The electrodes were employed to sense ascorbic acid in alkaline solution with a high sensitivity, 296 μAcm⁻² mM⁻¹, and good selectivity for eight kinds of disturbing reagents. We found that the ascorbic acid was oxidized irreversibly in solution. To match with the variation of the morphology, the sensitivity reached a maximum when the RuO_x segregated with a nano-crystalline feature. We find that the substrate oxidized as the deposited RuO_x grew thicker. The feature of the deposited RuO_x changed from nano-particles to small islands resulting from the wetting effect of the substrate oxide, NiO; meanwhile the sensitivity decreased dramatically. The endurance of the RuO_x/Ni electrode also showed a good performance after 38 days of successive test.

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1. Introduction

Ascorbic acid (H₂A), also known as vitamin C, has always been important because it is indispensable to human metabolic functions. Insufficient supply of H₂A in body causes symptoms of scurvy but excess supply of H₂A results in stomach convulsions. H₂A helps to promote healthy cell development and normal tissue growth; it helps the healing of injuries and burns.

Ascorbic acid was difficult to measure directly because of its characteristics; it is water soluble, antioxidant, and not stored in the body. Various H₂A sensors have been developed and have delivered versatile functions and various advantages. The typical ISFET, *i.e.* ion-sensitive field effect transistor, possesses a high stability, and a

fast response; but the lithography for the transistor structure is very costly (Martinoia et al., 2005). An optical H₂A sensor can detect H₂A in-situ without disturbance, but its usefulness is limited by environmental factors, *e.g.* temperature and optical sources (Jain et al., 1995). A conductometric sensor can be operated with ease but its sensitivity, selectivity, and accuracy deviate from that of the ideal sensor considerably (Ivanow et al., 2006). A potentiometric sensor can operate under extreme conditions in its miniature working area; but the typical operator cannot tolerate its slow response and the ionic noise induced by other ions in the solution (Amini et al., 2001). An amperometric sensor conquers the above disadvantages. It is usually designed as a laminate structure, with a film and a substrate, in which the film is proportionally sensitive to specific chemicals. Not only does the amperometric sensor detect a wide range of concentrations, but it also displays a fast response compared to other H₂A sensors (Weng et al., 2010).

Lately ceramic-modified material, oxide of metal, prevailed over

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the electrode development, and it was capable of improving the electron transfer between the electrode surface and the analyte, ascorbic acid (Arenas et al., 2010). The modified oxide on the surface of the electrode not only reduced the overvoltage of ascorbic acid oxidation, shifting the oxidation potential but also enhanced the peak current considerably (Pisoschi et al., 2014). Ruthenium oxide has received much attention for its electrochemical activity (Zheng et al., 1995). Ruthenium oxide shows excellent electrocatalytic characteristics for reactions found in the Fischer-Tropsch process and fuel cells (Ashcroft et al., 1990). By itself, ruthenium oxide can't represent its catalysis when no hydration occurs on its surface. As long as the ruthenium oxide precipitates, it often plays an aggressive role to increase the response. Nickel is a metal that is sensitive to H_2A . This research employed nickel as a matrix. The relative electrochemical reaction was enhanced by laminating with different thicknesses of ruthenium oxide. Under the investigation of microstructure variation, the sensing mechanism is connected with the preferred texture of the coated modifier. This research advances the state of the art by increasing the sensor's sensitivity i.e. response current per electrode area per mol of test solution, and selectivity, i.e. response to disturbing reagents. Also we not only explored the electrochemical reaction mechanism on the electrode, but investigated the microstructure variation of the electrode itself.

2. Experiments

2.1. Preparation of the RuO_x/Ni electrode

Nickel slices were prepared to serve as substrates by the following process. Slices of nickel with dimension $1\text{ cm} \times 6.5\text{ cm} \times 0.05\text{ cm}$ were ground and polished to remove their native oxide. These slices were cleaned with acetone to clear the remaining organics and then rinsed in de-ionized water ultrasonically for 10 min to remove the rest of the acetone. Finally these slices were dried in a vacuum oven to evacuate the residual water.

The polished nickel slices were modified in the following way. The polished and cleaned slices were immersed in a tank of solution, 0.1 M $RuCl_3$ (Seedchem) and simultaneously vibrated in an ultrasonic bath for 10 min. Then the $RuCl_3$ -wetted slices were dried and sintered in a furnace. At first, the remained water was evaporated at $100\text{ }^\circ\text{C}$ for 10 min. Then the residual $RuCl_3$ was decomposed and further oxidized by introducing oxygen at $450\text{ }^\circ\text{C}$ for 4 h. A thin layer of ruthenium oxide was thus deposited on the nickel substrate. In the same way, the ruthenium oxide was laminated layer by layer. The assemblies of ruthenium oxide/Ni (RuO_x/Ni) were subjected to a scanning electron microscope (S-3000N, Hitachi Co. Ltd) equipped with EDS (EX-250, Horiba Co. Ltd.) for investigation of morphology and composition. The phase of the modified electrode was identified with an x-ray diffractometer (X'Pert Pro MRD, PANalytical).

2.2. Electrochemical test

The three-electrode electrochemical cell was used as sensing system. The modified electrode, RuO_x/Ni , were configured as electrodes and subjected to 0.1M KOH solution in which $-OH$ groups provided the electrochemical features (Trasatti, 1990). A platinum sheet and an $Ag/AgCl$ electrode were employed as the counter and reference electrode, respectively. $L(+)$ ascorbic acid (Acros, 99%) was blended in deionized water as the major sensing material. An EG&G 273A potentiostat with m270 Electrochemical Analysis was used to control potential and record the corresponding current. All potentials were referred to the reference electrode. After choosing the properly applied potential at which the mass transfer of ascorbic acid to electrode surface was the rate-determining step,

the sensing process could be carried out. When the background current was stable, the desired amount of testing ascorbic acid was injected into the flask and the amperometric response current of the working electrode was recorded. To test its selectivity, the general disturbing reagents were employed as unknown, including oxalic acid anhydrous (SHOWA, 99%), sucrose (SHOWA, >99.9%), tartaric acid (SHOWA, 99%), D(-)-fructose (Acros, 99%), and uric acid (SHOWA, >99.9%).

3. Results and discussion

3.1. Microstructure investigation

Morphology variation revealed segregation of the ruthenium oxide on the substrate. Fig. 1 shows a series of morphologies for 0, 3, 7, and 9 layers of ruthenium oxide; all layers were deposited sequentially. Fig. 1(a) displays the features of a relatively smooth Ni substrate. In Fig. 1(b), a Ni substrate coated with three layers of ruthenium oxide shows a similar morphology to Fig. 1(a). This suggests that the lattice of the deposited ruthenium oxide matched with the lattice of the substrate. The deposited ruthenium oxide was blended with the Ni lattice as a form of solid solution. Fig. 1(c) shows a rough surface because many small cubic ruthenium oxide particles precipitated on the Ni electrode. Nowakowski and his co-workers found that RuO_2 presented a quasi-rectangular shape when it precipitated with sizes ranging from 8 to 14 nm (Nowakowski et al., 2008b). The more layers were made, the larger these grains were. Fig. 1(d) shows this effect with nine layers. This indicates that the ruthenium oxide no longer merged into the Ni lattice but segregated with a type of precipitate. This happened because the ruthenium oxide possessed a higher surface energy than the Ni substrate. Not only did the ruthenium oxide dewet the substrate, it also showed littered particles. A similar feature was also researched by Nowakowski and his coworker in another report (Nowakowski et al., 2008a). They found that the microstructure of the RuO_2 had significant effects on particle sizes. When the particles were small, the lattice of RuO_2 was expanded because dense point defects were introduced. These defects were able to serve as active sites for electrochemical reactions.

Phase identification confirmed the segregation of ruthenium oxide. Fig. 2 shows the diffraction patterns of the different thicknesses of ruthenium oxide on the Ni substrate. Note that only Ni peaks appeared for the assembly $RuO_x(3\text{ layers})/Ni$. This suggests that thin ruthenium oxide could be merged into the Ni lattice to show a similar pattern to that of the substrate, Ni. A lot of broadened peaks appeared on the pattern of $RuO_x(7\text{ layers})/Ni$. It is due to the nano-scaled crystalline of ruthenium oxide which possessed high surface energy, 1.14 Jm^{-2} for $RuO_2(110)$ and 1.40 Jm^{-2} for $RuO_2(100)$ (Kim et al., 2001). This high surface energy is apt to dewet the substrate; therefore, the deposited RuO_x condensed as nanoparticles and its diffraction pattern revealed a broadening feature. We briefly conclude that ruthenium oxide resolved in the nickel lattice when its thickness was thin; however, ruthenium oxide precipitated as the thickness grew over a critical threshold. Beyond the critical thickness, the ruthenium oxide no more merged with the Ni lattice as a solid solution, but it got clusters with a specific texture and thus a nano-crystalline form. Moreover, the matrix phase, Ni, competed with the ruthenium element to oxidize as NiO when the layer increased to nine layers as shown in the pattern of $RuO_x(9\text{ layers})/Ni$. Because the NiO formed on the surface, the surface energy increased from 1.78 Jm^{-2} for Ni (Murr, 1975) to 4.25 Jm^{-2} for NiO (Wolf, 1992). The deposited RuO_x tended to spread as layer, i.e. RuO_x got more space to develop as well-crystallized phase. Table 1 shows quantitative measurements of the segregated species. In Table 1, the ratio of Ru/O increased

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