An Efficient Electrochemical Sensor Driven by Hierarchical Hetero-Nanostructures Consisting of RuO$_2$ Nanorods on WO$_3$ Nanofibers for Detecting Biologically Relevant Molecules

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Abstract: By means of electrospinning with the thermal annealing process, we investigate a highly efficient sensing platform driven by a hierarchical hetero-nanostructure for the sensitive detection of biologically relevant molecules, consisting of single crystalline ruthenium dioxide nanorods (RuO$_2$ NRs) directly grown on the surface of electrosyn spun tungsten trioxide nanofibers (WO$_3$ NFs). Electrochemical measurements reveal the enhanced electron transfer kinetics at the prepared RuO$_2$ NRs-WO$_3$ NFs hetero-nanostructures due to the incorporation of conductive RuO$_2$ NRs nanostructures with a high surface area, resulting in improved relevant electrochemical sensing performances for detecting H$_2$O$_2$ and L-ascorbic acid with high sensitivity.

Keywords: ruthenium dioxide; tungsten trioxide; nanofibers; nanorods; electrochemical sensors

1. Introduction

Recently, a variety of metal oxide nanostructures have been extensively utilized as efficient electrode substances owing to their outstanding electrocatalytic properties. Among them, ruthenium dioxide (RuO$_2$) has been well described as one of the best electrocatalysts for diverse energy related applications, such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and supercapacitors because of its high electric conductivity, catalytic activity, and thermal stability [1–3]. Especially, RuO$_2$ has been used as an efficient electrode system for supercapacitors owing to its excellent charging-discharging behavior [1,4–8]. Generally, RuO$_2$ as a promising catalytic material is often used in the forms of hybrid structures or alloys with other abundant transition metals in consideration of the relatively high cost of RuO$_2$. Thus, there have been previous reports regarding the use of RuO$_2$ nanostructures with other metal oxides as supercapacitors [9–12], and biosensing applications [1–3,13,14].

Tungsten trioxide (WO$_3$) nanostructures have been also extensively studied in various applications due to its earth-abundance, high durability, and chemical stabilities in aqueous acid media, as well as good electrochemical conductivity [15–18]. Thereby it has been developed as a catalyst for the hydrogen evolution reaction (HER) and supercapacitors in an acidic solution [19–22]. WO$_3$ also constitutes composites with other novel metals like Pt [23–26], Ir [17,23,27], and Ru [16,28–30], or supporting materials.

Nanostructured catalysts are applied to nonenzymatic electrochemical biosensors. Electrochemical properties can be enhanced from the increase of active surfaces. The detection of hydrogen peroxide (H$_2$O$_2$) is important in not only biomedical and environmental applications, but also in the enzymatic
system [31]. While ascorbic acid (AA) has an important role in the physiological function of organisms, a deficiency of AA causes several diseases [32,33]. Therefore, the detection and accurate quantification of target material with selectivity is highly required.

In this study, we introduce a facile fabrication of hybrid nanostructures consisting of single crystalline RuO$_2$ nanorods on electrospun WO$_3$ nanofibers by utilizing electrospinning and thermal annealing processes. In addition, the fundamental electrochemical performances of RuO$_2$ nanorods-WO$_3$ nanofibers (RuO$_2$ NRs-WO$_3$ NFs) are carefully investigated, which confirm their characteristics of fast electron-transfer reactions and possibility as a catalytic sensing platform for detecting L-ascorbic acid (AA) and hydrogen peroxide (H$_2$O$_2$) in phosphate buffered solution (PBS).

2. Materials and Methods

Tungsten chloride (WCl$_6$, ≥ 99.9% true metal basis), ruthenium chloride hydrate (RuCl$_3$·xH$_2$O, 99.98% trace metal basis), poly(vinyl pyrrolidone) (PVP, MW = 1,300,000), N,N-dimethylformamide (DMF), potassium ferricyanide ([K$_3$[Fe(CN)$_6$]]), L-ascorbic acid (AA), 4-acetamidophenol (AP), dopamine hydrochloride (DA), uric acid (UA), D-(+)-glucose, hydrogen peroxide (H$_2$O$_2$, 35 wt% solution in water), sodium phosphate monobasic, and sodium phosphate dibasic were supplied by Sigma Aldrich (St. Louis, MO). Commercial Pt/C and Ir/C (both of them were 20 wt% each metal loading on Vulcan XC-72) were obtained from E-TEK Company. Sulfuric acid (H$_2$SO$_4$) and acetic acid were provided by Ducksan (Korea). Sodium hydroxide (NaOH) was purchased from Daejung (Korea). Deionized water with resistivity ≥ 18 MΩ·cm was used in all processes.

First, WO$_3$ nanofibers were synthesized by electrospinning and thermal annealing process according to the reported method [23]. To prepare electrospinning solution, 1.5 g WCl$_6$ were dissolved in 10.549 mL DMF with 1.25 g PVP and 0.191 mL acetic acid. After being stirred overnight, the solution was loaded into syringe and applied to the needle of the electrospinning system (Nano NC ESR 200R2). The needle was connected to a voltage power supply (applied voltage = 17.5 kV) at a flow rate of 5 µL/min, and the distance from needle tip to aluminum plate to collect as spun NFs was 15 cm. The collected electrospun NFs were calcinated at 500 °C for 1 h under a mixed gas atmosphere of 80 sccm of He and 10 sccm of O$_2$ with ramping rate of 1 °C/min.

Ruthenium hydroxide (Ru(OH)$_3$) precursor was prepared by a precipitation process via the acid-base reaction with controlling pH of aqueous solution. The pH of the final precursor solution at about pH 10 was carefully achieved by slowly dropping 0.1 M NaOH dilute solution into 5 mM RuCl$_3$·xH$_2$O aqueous solution [2,13]. After precipitation, the precursor solution was washed five times with deionized water, and then re-dispersed in 2–3 mL pure deionized water again. To grow RuO$_2$ NRs on WO$_3$ NFs, 2 mg of WO$_3$ NFs was dispersed into 1 mL deionized water and then mixed with 1 mL Ru(OH)$_3$ precursor solution. After sonication for 30 min, the mixed solution was directly dropped on the center of Si wafer. WO$_3$ nanofibers containing Ru(OH)$_3$ precursors loaded on the Si wafer was placed into the center of a furnace and calcined at 300 °C for 5 h in air. The furnace was then allowed to cool to room temperature.

The surface morphology of as-grown products was examined by field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F). The detailed crystal structures were also investigated by a high-resolution transmission electron microscopy (HRTEM, Cs-corrected STEM, JEOL JEM-2100F) instrument equipped with selected area electron diffraction (SAED) micrographs and elemental EDX mapping with a Tecnai-F20 system operated at 200 kV. Additionally, high resolution X-ray diffraction measurement (XRD; Bruker D8 DISCOVER, Cu Kα radiation), and X-ray photoelectron spectroscopy (XPS; Theta Probe AR-XPS System. Al Kα radiation) were performed to investigate the crystal structure and surface binding energies of as-grown RuO$_2$ NR-WO$_3$ NFs.

For electrochemical measurements, a three-electrode system was used with a modified glassy carbon (GC) electrode (3 mm in diameter), a saturated calomel electrode (S.C.E.), and a coiled Pt wire (1 mm in diameter, length immersed in a solution ~ 10 cm) as the working electrode, the reference electrode, and the counter electrode, respectively. All electrochemical experiments conducted with
CHI 650E workstation (CH Instruments) and BAS100B (BAS Inc.). To modify the surface of a GC electrode with synthesized nanomaterials, 2 mg of RuO$_2$ NR-WO$_3$ NFs was suspended in 1.0 mL deionized water. Subsequently, 10 µL of the solution were dropped onto the GC electrode surface three times. Then, 10 µL of 0.05 wt% Nafion solution were loaded onto the modified GC electrode surface. Cyclic voltammetry (CV) measurements was used for analyze the capacitive behavior in 1 M H$_2$SO$_4$. For sensing experiments, linear sweep voltammetry (LSV) was also used with rotating disk electrode (RDE) at a scan rate of 5 mV s$^{-1}$ with rotating speed of 1600 rpm, and amperometry measurements were used in 0.1 M phosphate buffered saline (PBS) at physiological condition pH (7.4).

3. Results and Discussion

3.1. Synthesis of Hybrid Nanostructures of RuO$_2$ Nanorods on Electrospun WO$_3$ Nanofibers

Figure 1A,B show FE-SEM images of WO$_3$ NFs annealed at 500 °C. The calcined WO$_3$ NFs revealed a very fine structure and the diameter of the fibers was around 200 nm. On the other hand, after the heat treatment of the mixed solution composed of Ru(OH)$_3$ precursors and WO$_3$ NFs at 300 °C for 5 h, it is readily identified that RuO$_2$ NRs were directly grown on the electrospun WO$_3$ NFs as shown in Figure 1C,D. Figure 1D represents the as grown RuO$_2$ NRs covering the entire surface of WO$_3$ NFs. The lateral dimension of RuO$_2$ NRs is estimated to be about 40 nm and the length up to 300 nm. Careful EDS measurements indicate that the atomic ratio of Ru to W is confirmed as 45:55. According to our previous real-time study by in situ synchrotron XRD, a simple recrystallization process by thermal annealing might be responsible for the growth mechanism of RuO$_2$ NRs. It was carefully suggested that Ru diffusion to the amorphous nanoparticles followed by diffusion to the growing surface of the nanorod plays an essential role in the growth of RuO$_2$ NRs in oxygen ambient, which is supported by the nucleation theory [34].

![Figure 1](image_url)  
*Figure 1. (A,B) SEM images of pure electrospun WO$_3$ nanofibers (WO$_3$ NFs). (C,D) SEM images of as grown RuO$_2$ nanorods on the electrospun WO$_3$ nanofibers (RuO$_2$ NRs-WO$_3$ NFs).*

Figure 2 represents XRD spectra and high resolution XPS spectra of composite RuO$_2$ NRs-WO$_3$ NFs and pure WO$_3$ NFs. XRD spectrum of pure WO$_3$ NFs in Figure 2B demonstrates that all peaks are closely matched with the monoclinic phase of WO$_3$ [19,35]. On the other hand, XRD spectrum of composite RuO$_2$ NR-WO$_3$ NFs confirms the same monoclinic phase WO$_3$ peaks including two major peaks at 27.1° and 34.8° corresponding to (110) and (101) crystallographic planes of tetragonal RuO$_2$ structure as displayed in Figure 2A [2,13]. To investigate the oxidation states of Ru, W, and O atoms, XPS measurements were performed. In Figure 2C, two separated binding energies at 35.1 eV and 37.3 eV are clearly identified as two spin-orbit states of W 4f$_{5/2}$ and W 4f$_{7/2}$, respectively, which indicates the oxidation state of +6 for W in WO$_3$ NFs [16,36]. Both high resolution Ru 3d and Ru
3p spectra were shown in Figure 2E,F. Although the peak position of Ru 3d_{3/2} is overlapped with C 1s [16,37], the oxidation state of Ru species is readily identified to Ru^{4+} based on the binding energies of 280.7 eV and 462.8 eV, indexed to Ru 3d_{5/2} and Ru 3p_{3/2}, respectively [37,38]. In addition, the peak at 530.5 eV of O 1s is associated with O^{2-} in RuO_2 and WO_3 metal oxides as shown in Figure 2D.

**Figure 2.** (A) XRD spectrum for RuO_2 NRs-WO_3 NFs (B) XRD spectrum for pure WO_3 NFs. (C–F) high resolution XPS spectra for RuO_2 NRs-WO_3 NFs, (C) W 4f, (D) O 1s, (E) Ru 3d, and (F) Ru 3p regions, respectively.

Figure 3 indicates TEM images and SAED pattern for a single WO_3 nanofiber covered with RuO_2 nanorods. As shown in Figure 3A,B, low-magnification TEM images show the high density of RuO_2 nanorods directly grown on the porous surface of WO_3 nanofiber. The SAED pattern shown in Figure 3E reveals the existence of many different crystalline phases in a WO_3 nanofiber. On the contrary, the fast Fourier transform (FFT) of the lattice-resolved image for a RuO_2 nanorod in Figure 3F represents highly ordered lattice fringes with a single crystal nature. The values of lattice spacing of adjacent planes are estimated by about 0.318 nm and 0.263 nm, corresponding to those of between the (110) planes and (101) for the tetragonal RuO_2, respectively. Furthermore, TEM-EDS element mapping analysis from the high-angle annular dark field (HAADF) STEM image shown in Figure S1 confirms the homogenous distribution of Ru, W, and O in distinct regions in the hierarchical nanostructure. W atoms exist on the backbone of the nanofibers, whereas Ru atoms exclusively exist on the branched nanorods. Oxygen atoms exist both on the backbone of the nanofibers and branched nanorods. Thus, we successfully fabricate the high density of single-crystalline RuO_2 nanorods on WO_3 nanofibers by using a combination of an electrospinning process and a thermal annealing process. Our growth process thus provides a simple methodology for the fabrication of highly efficient electrocatalysts.

3.2. Electrochemical Properties for Capacitive Behaviors of RuO_2 NRs-WO_3 NFs

The general electrochemical activities of RuO_2 NRs-WO_3 NFs and WO_3 NFs were examined by CV in 10 mM [Fe(CN)_6]^{3−}/[Fe(CN)_6]^{4−} aqueous solution containing 1 M KCl. Figure S2 displays CV curves of RuO_2 NRs-WO_3 NFs and WO_3 NFs at a scan rate 100 mV s^{−1}. Voltammetric current peaks at RuO_2 NRs-WO_3 NFs are reversible, while those of WO_3 NFs are quasi-reversible. It seems to be ascribed to that RuO_2 NRs-WO_3 NFs allow very facile heterogeneous electron transfer kinetics with high electric...
conductivities in contrast to WO$_3$ NFs. Moreover, RuO$_2$ NRs-WO$_3$ NFs show a much larger charging current in CV than WO$_3$ NFs.

To characterize the charging behavior of the synthesized materials, CV was measured for a potential range from 0.1 V to 0.9 V (vs. S.C.E.) in 1 M H$_2$SO$_4$ as seen in Figure 4. Figure 4A shows CV results comparing RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs at a scan rate 100 mV s$^{-1}$. It supports the enhanced capacity of RuO$_2$ NRs-WO$_3$ NFs as the RuO$_2$ NRs were grown on WO$_3$ NFs. To examine the charging performance, the average specific capacitance values ($C_{sp}$, F g$^{-1}$) were calculated with the following Equation (1) using CV curves shown in Figure 4B.

$$C_{sp} = \frac{1}{2 \times v \times \Delta m \times \Delta V} \int IdV$$

where $v$ is the scan rate (V s$^{-1}$), $\Delta m$ is the weight of electrode materials, $\Delta V$ is the potential range, and $IdV$ is the area under CV curve [39]. At the scan rate of 10 mV s$^{-1}$, the $C_{sp}$ values of the synthesized materials, RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs, are 98.15 F g$^{-1}$ and 0.95 F g$^{-1}$, respectively. The $C_{sp}$ of RuO$_2$ NRs-WO$_3$ NFs is obviously 103-fold higher than that of WO$_3$ NFs as shown in Figure 4C.

![Figure 3. (A,B) low magnification TEM images for RuO$_2$ nanorods on a single WO$_3$ nanofiber. (C) The high resolution TEM image for RuO$_2$ nanorods on a single WO$_3$ nanofiber. (D) The bright field TEM image for RuO$_2$ nanorods on a single WO$_3$ nanofiber. (E,F) SAED pattern for a WO$_3$ nanofiber and fast Fourier transform (FFT) of the lattice-resolved image for a single RuO$_2$ nanorod.](image-url)
As the scan rate increases, $C_{sp}$ becomes smaller and the $C_{sp}$ of RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs decreased down to 57% and 42%, respectively, while increasing the scan rate from 10 mV s$^{-1}$ to 200 mV s$^{-1}$. This additionally indicates the successful decoration of WO$_3$ NFs with RuO$_2$ NRs forming the hierarchical hetero-nanostructures.

Electrochemical impedance spectroscopy (EIS) was also employed to examine the electrochemical behavior of RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs. EIS measurement was carried out at 0.5 V (vs. S.C.E.) under the same condition of CV experiments with a frequency range of 0.1 Hz–1000 kHz as shown in Figure S3. The Nyquist plot of RuO$_2$ NRs-WO$_3$ NFs was closer to a vertical line than that of WO$_3$ NFs, exhibiting nearly pure capacitive behavior of RuO$_2$ NR-WO$_3$ NFs [1,40]. The stability of RuO$_2$ NRs-WO$_3$ NFs for capacitance was demonstrated by monitoring the change of $C_{sp}$ during repeated CV cycles as depicted in Figure 4D. RuO$_2$ NRs-WO$_3$ NFs excellently maintained about 96% of its original $C_{sp}$ for the 1000 CV cycles at a scan rate of 100 mV s$^{-1}$.

### Figure 4.
Capacitive current measurements in 1 M H$_2$SO$_4$ solution for (A) RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs at a scan rate 100 mV s$^{-1}$, and (B) RuO$_2$ NRs-WO$_3$ NFs with varying the scan rate from 10 mV s$^{-1}$ to 200 mV s$^{-1}$. (C) Changes of specific capacitance ($C_{sp}$) values of RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs as a function of the CV scan rate (from 10 mV s$^{-1}$ to 200 mV s$^{-1}$). (D) Plot of the $C_{sp}$ values of RuO$_2$ NRs-WO$_3$ NFs depending on the number of repeated CV cycles in 1 M H$_2$SO$_4$.

### 3.3. Applications to Electrochemical Sensing of AA and H$_2$O$_2$

The electrochemical properties of RuO$_2$ NRs-WO$_3$ NFs for AA oxidation were also studied. LSV measurements in 0.1 M PBS were used for examining the oxidations of various biomaterials such as AA, DA, UA, AP, and glucose. The chosen concentrations are slightly above the physiological concentrations. As shown in Figure 5A, AA oxidation started to occur from the most negative potential compared with other biomaterials. Amperometric measurements of RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs were conducted at 0 V (vs. S.C.E.) which possibly allow for the oxidation of AA only, excepting for the other tested biomolecules as seen in the LSV results of Figure 5A.
As observed in Figure 5B, the anodic currents of both electrodes were increased linearly with the concentration of AA increased from 5 μM to 2 mM. Also, the calibration curves based on the amperometric data were depicted in inset of Figure 5B. The sensitivity of RuO$_2$ NRs-WO$_3$ NFs (171.7 μA mM$^{-1}$ cm$^{-2}$, $R^2 = 0.9990$) was surprisingly increased by 244 times compared to that of WO$_3$ NFs (0.704 μA mM$^{-1}$ cm$^{-2}$, $R^2 = 0.9990$). Most of the typical biological samples are complex, having various oxidizable species, so selectivity to a targeted analyte is an essential requirement for any sensor. In Figure 6A, current responses for AA oxidation were stable against the additions of 0.1 mM AP, 0.1 mM UA, 0.1 mM DA and 5 mM glucose at 0 V. Additionally, the stability of RuO$_2$ NRs-WO$_3$ NFs was measured by monitoring the change of current at 0 V in 0.1 M PBS containing 0.3 mM AA. The amperometric response of RuO$_2$ NRs-WO$_3$ NFs retained 96% of the initial current level during over a 4200-s measurement in Figure 6B, supporting its excellent stability. Table 1 summarizes the properties of RuO$_2$ NRs-WO$_3$ NFs in comparison with other Ru-based materials used as AA sensors.

**Figure 5.** (A) Background-corrected LSVs of RuO$_2$ NRs-WO$_3$ NFs obtained in 0.1 M PBS (pH 7.4) independently containing one of 0.1 mM AA, 0.02 mM DA, 0.1 mM AP, 0.02 mM UA, 5 mM glucose (scan rate of 5 mV s$^{-1}$; and rotating speed of 1600 rpm). (B) Amperometric current responses of RuO$_2$ NRs-WO$_3$ NFs and WO$_3$ NFs for successive AA standard solution injections to increase the AA bulk concentration from 5 μM to 2 mM in 0.1 M PBS (pH 7.4) with $E_{app} = 0$ V (vs. S.C.E.). The inset: The calibration curves showing the current responses vs. concentration.

**Figure 6.** (A) Amperometric response of RuO$_2$ NRs-WO$_3$ NFs to sequential additions of 0.3 mM AA, 0.1 mM AP, 0.1 mM UA, 0.1 μM DA, 5 mM glucose and 0.6 mM AA to 0.1 M PBS (pH 7.4) with $E_{app} = 0$ V (vs. S.C.E.). (B) Continuous amperometric response of RuO$_2$ NRs-WO$_3$ NFs to 0.3 mM AA in 0.1 M PBS during 4200 s with $E_{app} = 0$ V (vs. S.C.E.).
Table 1. Comparison of the analytical performances of previous reported Ru-based AA sensors.

| Electrodes                  | Methods      | Solutions          | Potential /V | Sensitivity /µAmM⁻¹ cm² | Linear Range /µM |
|-----------------------------|--------------|--------------------|---------------|--------------------------|-----------------|
| RuO₂ NRs-WO₃ NFs           | Amperometry  | PBS (pH 7.4)       | 0             | 171.7                    | 5–2000          |
| RuO₂–Co₃O₄ hybrid nanotubes | Amperometry  | PBS (pH 7.4)       | 0.05          | 204                      | ~500            |
| RuO₂NWs–TiO₂NFs            | Amperometry  | PBS (pH 7.4)       | 0.018         | 268.2                    | 10–1500         |
| hAu-Ru nanoshells          | Amperometry  | PBS (pH 7.4)       | 0.05          | 426                      | 5–2000          |
| AC-RuON-GCE                | DPV          | PBS (pH 7.0)       | −0.053        | 85.9                     | 47–181.8        |
| Screen-printing RuO₂       | Amperometry  | PBS (pH 7.4)       | 0.058         | 2.79                     | 0–4000          |

1 This work, ² Ref. [3], ³ Ref. [13], ⁴ Ref. [41], ⁵ Ref. [42], ⁶ Ref. [43].

The catalytic effect of RuO₂ NRs-WO₃ NFs for H₂O₂ reduction was also measured. Figure 7A shows overlaid LSV results of RuO₂ NRs-WO₃ NFs and WO₃ NFs. It presents clearly that H₂O₂ reduction at RuO₂ NRs-WO₃ NFs starts from a much less negative potential with much greater reduction current level than that at WO₃ NFs. In fact, the cathodic current level measured at −0.2 V (vs. S.C.E.) was more greatly increased for RuO₂ NRs-WO₃ NFs than WO₃ NFs in response to the successive increase of H₂O₂ concentration (Figure 7B). Inset of Figure 7B shows the calibrated current vs concentration with good linearity. Obtained sensitivities from the calibration curves are 619.7 µAm M⁻¹ cm⁻² (R² = 0.9960), and 5.5 µAm M⁻¹ cm⁻² (R² = 0.9384) for RuO₂ NRs-WO₃ NFs and WO₃ NFs, respectively. Sensitivity of RuO₂ NR-WO₃ NFs is 112-fold higher than the value of WO₃ NFs, and therefore it supports the enhanced activities of RuO₂ NRs-WO₃ NFs toward H₂O₂ reduction. The H₂O₂ reduction current instead of the oxidation current was monitored to sense H₂O₂ in order to avoid the interference from many oxidizable species generally present in biological systems. Figure S4 represents the selectivity of RuO₂ NRs-WO₃ NFs for H₂O₂ reduction. The current responses of RuO₂ NRs-WO₃ NFs at −0.2 V (vs. S.C.E.) for H₂O₂ reduction were obvious; however, there were no noticeable responses to the successive injections of other biological materials: 0.1 mM AA, 0.1 mM UA, 0.1 µM DA, 5 mM glucose, 0.1 mM AP, and 30 µM O₂. RuO₂ NR-WO₃ NFs show relatively excellent catalytic activities for H₂O₂ reduction compared to other previous Ru-based materials as compared in Table 2. RuO₂ NRs-WO₃ NFs for measuring H₂O₂ reduction current was less stable than that for AA oxidation. In fact, H₂O₂ reduction current measured at −0.2 V was decreased to ~60% of the initial current level after 4200-s continuous measurement (data not shown).
Figure 7. (A) Background-corrected LSVs of RuO2 NRs-WO3 NFs and WO3 NFs obtained in 0.1 M PBS (pH 7.4) containing 0.5 mM H2O2 with a scan rate of 5 mV s−1, at an electrode rotating speed of 1600 rpm. (B) Amperometric current responses of RuO2 NRs-WO3 NFs and WO3 NFs to successive H2O2 injections from 0.005 mM to 2 mM in 0.1 M PBS (pH 7.4) at −0.2 V (vs. S.C.E.); the inset: corresponding calibration curves.

Table 2. Summary of the analytical performances of reported Ru-based H2O2 sensors.

| Electodes                  | Methods    | Solutions   | Potential /V | Sensitivity /µA mM−1 cm−2 | Linear Range /µM |
|----------------------------|------------|-------------|--------------|---------------------------|-----------------|
| RuO2 NRs-WO3 NFs           | Amperometry| 0.1 M PBS   | −0.2         | 619.7                     | 5–2000          |
| RuO2-ReO3 (0.11)           | Amperometry| 0.1 M PBS   | −0.2         | 667.8                     | 0–5000          |
| RuO3NNS-TiO2 NRS           | Amperometry| 0.05 M PBS  | 0            | 53.8                      | 1–1000          |
| RuO2 NWs-Rh2O3 NFs         | Amperometry| 0.05 M PBS  | 0.12         | 283.1                     | 0–1000          |
| HRP/Chi-GAD/RuNPs          | Amperometry| Saturated PBS| −0.3        | 0.798                     | 5090–15,000     |
| Nafion-RuO2-AuNP film      | Amperometry| PBS         | −0.4         | 15.44                     | 0.001–30,000    |

1 This work, 2 Ref. [1], 3 Ref. [2], 4 Ref. [14], 5 Ref. [44], 6 Ref. [45]. HRP: horseradish peroxidase, Chi: chitosan, GAD: glutaraldehyde

4. Conclusions

We report the successful fabrication of single crystalline RuO2 nanorods on WO3 nanofibers by electrospinning and calcination. Microscopic and spectroscopic measurements such as SEM with EDS, XRD, and XPS were used to characterize the structure and composition of RuO2 NRs-WO3 NFs. The RuO2 NRs-WO3 NFs showed improved electrocatalytic activities over WO3 NFs through a series of electrochemical measurements. In 1 M H2SO4 solution, RuO2 NRs-WO3 NFs represent a higher Csp, 98.15 F g−1, by 103-fold with good stability and a sharper slope than pure WO3 NFs. Additionally, the RuO2 NRs-WO3 NFs have dramatically enhanced sensing abilities, in accordance with 224 times (171.7 µA mM−1 cm−2) sensitivity for AA oxidation, and 112 times (619.7 µA mM−1 cm−2) sensitivity for H2O2 reduction, respectively, compared to those of pure WO3 NFs. These results thus suggest that RuO2 NRs-WO3 NFs could be a promising candidate electrocatalyst for the fabrication of an efficient electrochemical sensor due to its highly effective electrochemical performance.

Supplementary Materials: The followings are available online at http://www.mdpi.com/1424-8220/19/15/3295/s1, Figure S1: EDS elemental mappings, Figure S2: Cyclic voltammograms, Figure S3: Nyquist plots, Figure S4: Amperometric response.

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