Article

Electrocatalytic Properties of a BaTiO₃/MWCNT Composite for Citric Acid Detection

Siraprapa Pitiphattharabun ^{1,2}, Nicha Sato ¹ , Gasidit Panomsuwan ^{1,3} and Oratai Jongprateep ^{1,3,*}

¹ Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand; siraprapa.pi@ku.th (S.P.); nicha.sat@ku.th (N.S.); fenggd@ku.ac.th (G.P.)

² Program of Sustainable Energy and Resources Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

³ International Collaborative Education Program for Materials Technology, Education, and Research (ICE-Matter), ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net), Bangkok 10330, Thailand

* Correspondence: fenggtj@ku.ac.th; Tel.: +66-27970999

Abstract: Although barium titanate (BaTiO₃) shows prominent dielectric properties for fabricating electronic devices, its utilization in electrochemical applications is limited. Thus, this study examined the potential of a BaTiO₃-based composite in the detection of a food additive, i.e., citric acid. First, a submicron-scale BaTiO₃ powder was synthesized using the solution combustion method. Then, a BaTiO₃/multiwalled carbon nanotube (MWCNT) composite was hydrothermally synthesized at BaTiO₃:MWCNT mass ratios of 1:1 and 2:1. This composite was used as a working electrode in a nonenzymatic sensor to evaluate its electrocatalytic activity. Cyclic voltammetric measurements revealed that the BaTiO₃/MWCNT composite (2:1) exhibited the highest electrocatalytic activity. Reduction reactions were observed at applied voltages of approximately 0.02 and −0.67 V, whereas oxidation reactions were detected at −0.65 and 0.47 V. With acceptable sensitivity, decent selectivity, and fair stability, the BaTiO₃/MWCNT composite (2:1) showed good potential for citric acid detection.

Keywords: solution combustion synthesis; BaTiO₃; electrochemical sensor; citric acid

Citation: Pitiphattharabun, S.; Sato, N.; Panomsuwan, G.; Jongprateep, O. Electrocatalytic Properties of a BaTiO₃/MWCNT Composite for Citric Acid Detection. *Catalysts* **2022**, *12*, 49. <https://doi.org/10.3390/catal12010049>

Academic Editor: Jin-Song Hu

Received: 23 November 2021

Accepted: 29 December 2021

Published: 2 January 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Citric acid is a soluble organic substance naturally found in citrus fruits. In the human body, it acts as an antioxidant as well as a buffering and mineral delivery agent and participates in the glycolytic process. Moreover, it inhibits the growth of calcium oxalate and calcium phosphate stones, preventing urolithiasis and other kidney diseases. However, high concentrations of citric acid cause the erosion, softening, and damage of the tooth enamel [1,2]. According to Fiume et al., the safe threshold level of citric acid in human blood is ~0.13 mM. In addition to its natural functions, citric acid is used as a dietary supplement, as well as a food additive for preservation and flavor enhancement. Furthermore, it is used in cosmetics and medicine; however, severe skin irritation and breathing difficulties have been reported after using cosmetic products that contain high-concentration citric acid [3].

Based on this discussion, the detection of citric acid is essential, which can be achieved using several techniques, including high-performance liquid chromatography (HPLC) and capillary electrophoresis [4,5]. However, because of the requirements of high-cost instruments and experienced operators, these techniques are unsuitable for point-of-care testing applications. Furthermore, colorimetry, visible–near-infrared spectroscopy, and fluorescence spectroscopy have been used for citric acid detection [6–8]. However, colorimetry is unsuitable for detecting colorless samples [9]. In the presence of interference in the sample, a high noise signal may be detected in spectroscopic techniques. Alternatively, nonenzymatic electrochemical sensing techniques exhibit good simplicity, sensitivity, selectivity, reusability, and stability and thus can be used for the quantitative detection of

citric acid [10]. The electrochemical activity and performance of electrochemical sensors are often evaluated using cyclic voltammetry (CV) because of its simplicity, fast operation, low cost, and capability to analyze both organic and inorganic analytes [11,12].

Barium titanate (BaTiO_3) is a perovskite with unique piezoelectric, ferroelectric, and dielectric properties [13,14]. It generally comprises tetragonal and cubic phases; cubic BaTiO_3 exhibits paraelectric properties with a low dielectric constant, whereas tetragonal BaTiO_3 shows ferroelectric properties with a high dielectric constant [15]. BaTiO_3 has been widely used for fabricating microelectronic and optoelectronic devices such as actuators, capacitors, ferroelectric random-access memories, transducers, and electro-optic modulators [16,17]. However, although BaTiO_3 exhibits high stability and good electrocatalytic activity, its application in electrochemical sensing has been limited compared with dielectric applications [18].

BaTiO_3 can be synthesized using different methods such as solid-state reaction, coprecipitation, sol-gel, and spray pyrolysis techniques [19–22]. According to Ashiri and Clabel et al., BaTiO_3 synthesis using the solid-state reaction technique involves the milling process and requires a high temperature and a prolonged processing time [23,24]. Additionally, the sol-gel and coprecipitation techniques can afford good-quality powders. However, sol-gel reactions such as hydrolysis or polymerization generally require a long completion time. For the coprecipitation technique, an acid or a base is employed to control pH, possibly resulting in chemical residues. BaTiO_3 synthesis using the spray pyrolysis technique involves expensive equipment [25,26]. Jongprateep et al. and Khort et al. proposed the solution combustion method as a simple, low-cost, low-energy-consumptive, and robust method for preparing BaTiO_3 [27,28].

The electrocatalytic performance of oxides can be generally enhanced by adding Pt and its alloys; however, the high cost, low abundance, and toxicity associated with Pt and its alloys hinder their usage. Alternatively, carbonaceous materials, including graphene oxide (GO) and carbon nanotubes (CNTs), present low cost, high abundance, high stability, large surface-to-volume ratio, and enhanced electron-transfer ability; hence, they are a great alternative to Pt and its alloy to improve the electrocatalytic activity of electrochemical sensing materials [29–32].

Because of the high electrocatalytic performance of metal-oxide/multiwalled CNT (MWCNT) composites, they have been used as electrodes and studied extensively. Yusoff et al. observed clear micropores in a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) perovskite/MWCNT composite [33]. This composite achieved a higher specific surface area (SSA) than that of the pure BSCF perovskite and exhibited enhanced electrocatalytic oxygen reduction, which was attributed to the ability of MWCNTs to promote electron transfer and provide short-distance transportation between the ionic mass and charge. Chen et al. assessed the efficiency of BaTiO_3 /reduced GO (rGO) composites to enhance the performance of screen-printed carbon electrodes, obtaining a high current response when detecting ractopamine, a food additive with antibacterial properties used in the preservation of meat products [34].

This work aimed at exploring the potential of a BaTiO_3 /MWCNT composite as a citric acid sensor by investigating its electrocatalytic activities in the presence of citric acid. The chemical composition, microstructure, SSA, and optical characteristics of the BaTiO_3 powder prepared using the solution combustion method were also examined.

2. Results and Discussion

2.1. Phase Identification and Elemental Analysis of Synthesized Powder

The XRD pattern of the synthesized BaTiO_3 powder (Figure 1) revealed the presence of the cubic phase of BaTiO_3 (JCPDS No. 01-074-1964). The peak observed in the range of 43° – 48° could be an indicator of the BaTiO_3 phase. A single peak corresponding to the (200) plane indicated the cubic BaTiO_3 phase, whereas a peak splitting into the (002) and (200) planes suggested the tetragonal BaTiO_3 phase [35]. The XRD pattern revealed only a single peak of the (200) plane, indicating cubic-structured BaTiO_3 (Figure 1).

The Rietveld refinement was performed to gain additional insights into the structural information of the synthesized BaTiO_3 powder. The structural refinement revealed that the diffraction pattern of BaTiO_3 powder fitted well ($\chi^2 = 1.65$) with the cubic BaTiO_3 pattern in the crystallography open database (COD ID 1507757, space group Pm-3m) (Figure 2) [36,37]. The results showed that the refined lattice parameters a , b , and c were equal to 4.0014 Å.

The cubic and tetragonal phases of BaTiO_3 with distinct properties have been reported. According to Thanki et al., cubic BaTiO_3 shows better electrical conductivity than that of tetragonal BaTiO_3 [38]. Moreover, many studies have reported the potential of cubic BaTiO_3 in sensor applications. According to Petrovic et al., pseudocubic La-doped BaTiO_3 shows greater performance in gas sensing than that the tetragonal phase [39]. Chaudhari et al. reported the potential of nanocubic BaTiO_3 in the detection of liquid petroleum gas [40]. Based on the cubic structure, the synthesized BaTiO_3 powder may show the desirable sensing performance.

In addition to the BaTiO_3 peaks, the XRD pattern revealed a low-intensity peak assigned to barium carbonate (JCPDS No. 01-071-2394), whose formation can be associated with a chemical reaction between barium from the initial reagent and carbon from CO_2 or the combustion fuel. Khort et al. reported the formation of BaCO_3 via the reaction between barium oxide (decomposed from barium nitrate) and CO_2 , whereas Jongprateep and Tanmee observed the formation of BaCO_3 via the reaction between barium oxide and carbon from glycine [27,41].

The semiquantitative analysis of the BaCO_3 secondary phase was performed using Klug's equation, achieving the BaCO_3 content of 5.23 wt.%. Moreover, the quantitative analysis performed using the X'Pert HighScore Plus program indicated a comparable result of 5 wt.% BaCO_3 (Figure 3). A minimal content of BaCO_3 should not have considerable detrimental effects on the catalysis. Moreover, previous studies have reported that the presence of BaCO_3 could even enhance the catalytic process. According to Hong et al., the deposition of BaCO_3 on a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite afforded synergistic electrocatalytic activity [42]. Cao et al. reported that the presence of the BaCO_3 impurity phase in BaTiO_3 and LaFeO_3 yielded enhanced active sites, which contributed to the improved performance of ethanol sensing [43].

Figure 1. XRD patterns of the BaTiO_3 powder synthesized using the solution combustion method.

Figure 2. Rietveld refinement analysis of the BaTiO₃ powder.

Figure 3. (a) Quantitative analysis and (b) peak matching of the BaTiO₃ powder using the X'Pert HighScore Plus program.

Energy-dispersive X-ray spectroscopy (EDS) was performed to analyze the elemental composition of the synthesized powder. The elemental mapping and EDS spectra of the BaTiO₃ powder revealed that it was composed of barium (Ba), titanium (Ti), and oxygen (O). The atomic contents of Ba and Ti were 29.92 at.% and 26.96 at.%, respectively. To confirm the formation of BaTiO₃, the atomic ratio of Ba:Ti must be close to 1:1 [44–46]. The elemental analysis of the BaTiO₃ powder showed a Ba:Ti atomic ratio of 1.1:1, showing the presence of BaTiO₃ as the primary phase. As shown in Figure 4.

Figure 4. Energy-dispersive X-ray spectroscopy (EDS) results of BaTiO₃ (a) SEM image of mapping area, (b) EDS spectra, and elemental mapping of (c) barium (Ba), (d) titanium (Ti), and (e) oxygen (O).

2.2. Morphology of BaTiO₃ Powder

The SEM images of BaTiO₃ revealed irregular and cubic-shaped particles with a nonuniform particle size distribution (Figure 5a). The micrographs also revealed agglomeration among the particles. The average particle size and agglomerate size were 1.05 ± 0.51 and 3.42 ± 1.91 μm , respectively. According to Gao et al. and Khort et al., the agglomeration of the powder synthesized using the solution combustion method was triggered by the prolonged combustion period and high temperatures during the combustion and calcination processes [47,48].

SEM was also used to examine the BaTiO₃/MWCNT composite. The results revealed that the agglomerated BaTiO₃ particles were nonuniformly deposited in the MWCNT clusters (Figure 5b,c).

Figure 5. SEM images of (a) barium titanate (BaTiO₃), (b) BaTiO₃/MWCNT composite (1:1), and (c) BaTiO₃/MWCNT composite (2:1).

2.3. Specific Surface Area

The BET technique was used to determine the SSA of BaTiO₃. A large SSA provides several active sites for reactions, enhancing the catalytic activity and performance [49]. The SSA of the synthesized BaTiO₃ powder was low ($4.25 \text{ m}^2/\text{g}$), possibly attributed to the agglomeration of the BaTiO₃ particles, as revealed by SEM observations (Figure 5a). The SSA of MWCNTs was $315.28 \text{ m}^2/\text{g}$, suggesting additional active sites for reactions and enhanced electron transfer. Therefore, compared with pure BaTiO₃, the BaTiO₃/MWCNT composites potentially demonstrate superior electrocatalytic activity.

2.4. Electrocatalytic Activity

The sensing performance of MWCNTs, BaTiO₃, and BaTiO₃/MWCNT composites with BaTiO₃:MWCNT mass ratios of 1:1 and 2:1 in the presence of citric acid was examined using CV. The BaTiO₃/MWCNT composite-based electrode exhibited an oxidation peak at 0.43 V and reduction peaks at 0.02 and -0.77 V. For the BaTiO₃ electrode, a reduction reaction occurred at an applied voltage of -0.83 V. Two oxidation peaks were detected at applied voltages of approximately -0.65 and 0.47 V for the BaTiO₃/MWCNT composite-based electrode with BaTiO₃:MWCNT mass ratios of 1:1 and 2:1, whereas two reduction peaks were detected at approximately 0.02 and -0.67 V. The BaTiO₃/MWCNT composite (2:1) exhibited the highest peak current among the electrodes (Table 1).

BaTiO₃ showed low electrocatalytic activity and a minor reduction peak (Figure 6). Compared with BaTiO₃, BaTiO₃/MWCNT composite-based electrode showed superior electrocatalytic activity based on a higher peak current. This can be attributed to the large SSA of the CNTs, which provides additional active sites for reactions and enhances electron transfer. MWCNT-based materials have been used to fabricate cocatalysts and support many catalytic applications. According to Sato et al., carbon-supported metal-oxide composites show excellent electrocatalytic performance owing to the tuned electronic states of catalysts [50]. Therefore, combining carbon materials and metal oxides can enhance the catalytic process [51–53]. The synergistic effects of metal oxides and large-SSA carbon-based materials on electrocatalytic activities have been reported in many studies [54,55]. A similar observation was clearly evident in this study. The BaTiO₃/MWCNT composites showed excellent electrocatalytic activities based on the prominent reduction and oxidation peaks in the presence of citric acid.

Citric acid dissociates into various species during electrochemical reactions between metal and citric acid, including H₂Cit[−], HCit^{2−}, and Cit^{3−}. These species serve as initial precursors for the production of metal–citric acid complexes via redox reactions [56]. Similarly, electrochemical reactions occurring in BaTiO₃/MWCNTs can be expressed as follows:

Table 1. Peak currents of MWCNTs, BaTiO₃, BaTiO₃/MWCNT composite (1:1)-based electrode, and BaTiO₃/MWCNT composite (2:1)-based electrode in the presence of 500 µM citric acid.

Sample	Peak Current (mA)			
	−0.83 to −0.67 V	0.43 to 0.47 V	−0.70 to −0.65 V	0.02 V
MWCNTs	0.0111	0.0012	–	0.0003
BaTiO ₃	0.0057	–	–	–
BaTiO ₃ /MWCNTs (1:1)	0.0154	0.0016	0.0013	0.0006
BaTiO ₃ /MWCNTs (2:1)	0.0098	0.0057	0.0022	0.0024

Figure 6. Cyclic voltammogram of MWCNTs, BaTiO₃, BaTiO₃/MWCNT composite (1:1)-based electrode, and BaTiO₃/MWCNT composite (2:1)-based electrode in 500 µM citric acid at a scan rate of 100.0 mV/s.

Because the results revealed that the BaTiO₃/MWCNT composite (2:1)-based electrode showed the highest electrocatalytic activity in the detection of citric acid, this composite was selected for further electrocatalytic performance examinations.

The CV measurements of the BaTiO₃/MWCNT composite (2:1) in 500 µM citric acid were conducted at scan rates of 25.0–100.0 mV/s (Figure 7a). The cyclic voltammograms exhibited two prominent peaks, corresponding to oxidation reactions at applied voltages ranging from −0.74 to −0.65 V and 0.35 to 0.47 V. The peaks corresponding to reduction reactions were observed at applied voltages ranging from −0.67 to −0.51 V and 0.02 to 0.12 V. The correlation between the peak current and scan rate or square root of the scan rate was employed to determine the mechanism involved in electrocatalytic reactions. A good

linear relation ($R^2 > 0.75$) between the peak current and scan rate suggested the presence of an adsorption-controlled reaction, whereas a good linear relation between the peak current and square root of the scan rate indicated a diffusion-controlled reaction [57].

The relation between the peak current and scan rate and between the peak current and square root of the scan rate showed good linear relations with $R^2 = 0.981$ and 0.998, respectively (Figure 7b,c). Therefore, the mechanisms controlling the catalytic activities of the BaTiO₃/MWCNT composite (2:1) in citric acid were both adsorption-controlled reactions, associated with the concentration of analytes, and diffusion-controlled reactions, associated with electron transfer in the reactions.

Figure 7. (a) Cyclic voltammogram of the BaTiO₃/MWCNT composite (2:1)-based electrode at scan rates of 25–100.0 mV/s, (b) relation between the peak current and scan rate of reduction reactions, and (c) relation between the peak current and square root of the scan rate of reduction reactions in 500 μ M citric acid.

Generally, the relation between the current density and analyte concentration can be used to determine the sensitivity of an electrode. Herein, the sensitivity of the BaTiO₃/MWCNT composite (2:1)-based electrode for citric acid detection was evaluated using a calibration curve between the reduction current density and citric acid concentration. The results showed good linearity in the citric acid concentration range of 100–10,000 μ M (Figure 8), corresponding to the citrate concentration range in blood [3]. Table 2 presents the corresponding sensitivity values.

Table 2. Sensitivity of the BaTiO₃/MWCNT composite (2:1)-based electrode in 100–10,000 μ M citric acid.

Electrode	Concentration (μ M)	Equation (J)	Sensitivity (μ A μ M ⁻¹ mm ⁻²)	R ²
BaTiO ₃ /MWCNT composite (2:1)-based electrode	100–1000	$J = 0.00059C + 0.96912$	5.9×10^{-4}	0.9809
	1000–10,000	$J = 0.000068C + 1.46938$	6.8×10^{-5}	0.9869

Figure 8. Current density–analyte concentration calibration curves for the BaTiO₃/MWCNT composite (2:1)-based electrode in (a) 100–1000 µM and (b) 1000–10,000 µM citric acid measured at a scan rate of 100 mV/s for the reduction reaction at −0.67 V.

The lowest concentration that an electrode can detect at 95% level of confidence is generally referred to as the limit of detection (LOD), while the limit of quantification (LOQ) refers to the reliable lowest concentration of an analyte in detection. These values can be calculated as follows [58,59]:

$$\text{LOD} = 3.3\sigma/S \quad (2)$$

$$\text{LOQ} = 10\sigma/S, \quad (3)$$

where σ represents the standard deviation of blank and S represents the calibration curve slope at the lowest concentration range.

The LOD and LOQ of the BaTiO₃/MWCNT composite (2:1)-based electrode for citric acid were 0.061 and 0.18 mM, respectively. The performance of this electrode for the detection of citric acid is listed along with those reported in other studies in Table 3. The linear range and LOD values obtained in this study were within an acceptable range when compared with those obtained in the case of other electrochemical sensors, capillary electrophoresis, HPLC, fluorescence spectroscopic, and colorimetric techniques.

Table 3. Performance of various techniques in citric acid detection.

Detection Technique	Sensing Material	Linear Range (mM)	LOD (mM)	Ref.
Capillary electrophoresis with direct UV	-	2.6–91.3	0.0104	[60]
HPLC coupled with refractive index	-	0.2–3.1	0.172	[61]
HPLC/UV	-	1–10	0.51	[62]
Fluorescence spectroscopy	Fluorescent probe based on benzoindole derivatives	0.014–0.023	0.002967	[63]
Enzymic colorimetry	Citrate lyase, oxalacetate decarboxylase, pyruvate oxidase, 4-aminoantipyrine, and peroxidase	5×10^{-5} – 2×10^{-4}	1.3×10^{-5}	[64]
Electrochemical sensor with cyclic voltammetry	Co(II)-phthalocyanine	0.25–15	0.164	[65]
Electrochemical sensor with cyclic voltammetry	Polypyrrole-pentacyanonitrosylferrate/Pt	1–9	0.117	[66]
Electrochemical sensor with cyclic voltammetry	BaTiO ₃ /MWCNT composite (2:1)	0.1–10	0.061	This work

The selectivity of the BaTiO₃/MWCNT composite (2:1)-based electrode was examined via chronoamperometric measurements in the presence of citric acid, glutamate, nitrate, ascorbic acid, and nitrite. The electrode exhibited a prominent current signal of citric acid, demonstrating its good selectivity toward the target analyte (Figure 9).

Figure 9. Chronoamperogram of the BaTiO₃/MWCNT composite (2:1)-based electrode in 500 μM glutamate (Glu), 500 μM citric acid (CA), 500 μM nitrite, 500 μM ascorbic acid (AA), and 500 μM nitrite at an applied voltage of −0.67 V.

The stability of the BaTiO₃/MWCNT composite (2:1)-based electrode for citric acid detection was examined based on the peak current after repeating cycles (Figure 10). After 200 cycles, the peak current decreased by 23.31%, which was in the acceptable range for sensing materials reported by other researchers [67,68].

Figure 10. Peak current as a function of the number of cycles for the BaTiO₃/MWCNT composite (2:1)-based electrode in 500 μM citric acid at a scan rate 100 mV/s.

3. Materials and Methods

3.1. Synthesis of BaTiO₃ Powder

BaTiO₃ was synthesized using the solution combustion method by employing barium nitrate (Daejung, Daejung Chemicals & Metals Co., Ltd, Gyeonggi-do, Korea) and titanium dioxide (Sigma-Aldrich, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) as the initial reagents and dissolving them in nitric acid (RCI Labscan, RCI Labscan Limited, Bangkok, Thailand). First, a homogeneous aqueous solution containing barium and titanium ions was prepared. Then, glycine (Daejung, Daejung Chemicals & Metals Co., Ltd., Gyeonggi-do, Korea), functioning as a combustion fuel, was added to the solution. The combustion process was initiated at 400 °C, yielding a white powder that was collected and subsequently calcined at 900 °C for 3 h (Figure 11a). The reactions involved in the solution combustion synthesis of BaTiO₃ can be expressed using Equations (1) and (2).

The average yield of the solution combustion synthesis of BaTiO₃ for two replicates of the synthesis process was 75.8%.

Figure 11. Schematized procedures for synthesizing the (a) BaTiO₃ powder using the solution combustion method and (b) BaTiO₃/MWCNT composite-based electrode.

3.2. Preparation of BaTiO₃/MWCNT Composite as a Working Electrode

The BaTiO₃/MWCNT composite was prepared by mixing the synthesized BaTiO₃ powder and MWCNTs at BaTiO₃:MWCNT mass ratios of 1:1 and 2:1, followed by sonication for 30 min. The resulting mixture was dispersed in deionized water, autoclaved at 150 °C for 5 h, and dried overnight at 60 °C. The average yield of the BaTiO₃/MWCNT composite for two replicates of the synthesis process was 94.2%. The as-obtained BaTiO₃/MWCNT composite was dispersed in 99.9% ethanol (QR&C, Asia Chemie (Thailand) Co., Ltd., Chonburi, Thailand) at a composite:ethanol ratio of 1 mg:1 mL and sonicated for 30 min. Subsequently, 5 µL of the BaTiO₃/MWCNT composite suspension was dropped onto a glassy carbon electrode (Figure 11b).

3.3. Characterization

X-ray diffraction (XRD; X'Pert, Philips, PANalytical B.V., Almelo, Netherlands) was performed for phase identification via 2θ scanning from 20° to 80° with a step size of 0.02°. Moreover, the XRD pattern was used to examine the secondary phase based on Klug's equation [69,70]:

$$\text{Weight fraction} = \frac{\left(\frac{I_{\text{mix}}}{I_{\text{pure}}}\right) A_{\text{mix}}}{A_{\text{pure}} - \left(\frac{I_{\text{mix}}}{I_{\text{pure}}}\right) (A_{\text{pure}} - A_{\text{mix}})} \quad (6)$$

where I_{mix} and I_{pure} denote the integrated intensities of the secondary and pure phases, respectively, and A_{mix} and A_{pure} denote the corresponding mass absorption coefficients for the Cu K α radiation, respectively (A_{mix} and A_{pure} are 253.22 and 256.65 cm²/g) [36]. To confirm the results obtained using Klug's equation, the content of the secondary phase was also examined using the X'Pert HighScore Plus program version 3.0.

The XRD pattern of the synthesized powder was also used to conduct the Rietveld refinement on the FullProf Suite program version 7.40.

The morphology of the synthesized powder was characterized using scanning electron microscopy (SEM; Hitachi, SU3500, Hitachi High-Technologies Corporation, Tokyo, Japan). The SSA of the BaTiO₃ and MWCNT powders was examined using a surface area analyzer (Micrometrics, 3Flex, Micromeritics Instrument Corporation, Norcross, Georgia) using the Brunauer–Emmett–Teller (BET) technique. Before measuring the N₂ adsorption–desorption at 77 K, the powder was degassed at 200 °C for 3 h.

CV measurements were performed using a potentiostat (VSP, BioLogic, BioLogic Science Instruments Ltd., Seyssinet-Pariset, France) to evaluate the electrocatalytic activity of the BaTiO₃/MWCNT powder in a citric acid solution. To determine the peak

current, the measurements were replicated for at least five cycles. Ag/AgCl, Pt, and the BaTiO₃/MWCNT composite were used as the reference, auxiliary, and working electrodes, respectively. The applied voltage ranged from −1.4 to 1.4 V (Figure 12).

Figure 12. Experimental setup for CV measurements.

4. Conclusions

BaTiO₃ powder with average particle sizes of $1.05 \pm 0.51 \mu\text{m}$ was successfully synthesized using the solution combustion method. BaTiO₃/MWCNT composites at BaTiO₃:MWCNT mass ratios of 1:1 and 2:1 were prepared as BaTiO₃/MWCNT composite-based electrodes for citric acid detection. In the presence of citric acid, both BaTiO₃/MWCNT composite (1:1)- and BaTiO₃/MWCNT composite (2:1)-based electrodes underwent reduction reactions at 0.02 and −0.67 V. Oxidation reactions at −0.65 and 0.47 V were also observed. The BaTiO₃/MWCNT composite (2:1)-based electrode achieved the highest performance in citric acid detection, with sensitivities of 0.00059 and 0.000068 $\mu\text{A } \mu\text{M}^{-1} \text{ mm}^{-2}$ in citric concentration ranges of 100–1000 and 1000–10,000 μM , respectively. The LOD of the BaTiO₃/MWCNT composite (2:1)-based electrode was 0.061 mM. Owing to the good electrocatalytic performance, including an acceptable sensitivity, LOD, selectivity, and stability, BaTiO₃/MWCNT composites demonstrated great potential for applications in citric acid detection.

Author Contributions: Conceptualization, S.P., N.S. and O.J.; methodology, S.P. and N.S.; software, S.P.; validation, O.J. and G.P.; formal analysis, S.P. and O.J.; investigation, O.J. and G.P.; resources, O.J. and G.P.; data curation, S.P. and O.J.; writing—original draft preparation, S.P. and O.J.; writing—review and editing, O.J. and G.P.; visualization, O.J.; supervision, O.J.; project administration, O.J.; funding acquisition, O.J. and G.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Kasetsart University Research and Development Institute (KURDI) and ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net).

Data Availability Statement: Data sharing is not applicable to this article.

Acknowledgments: The authors would like to express their sincere gratitude to Kasetsart University Research and Development Institute (KURDI) and ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net) for financial support. The Department of Materials Engineering, Faculty of Engineering, Kasetsart University, is also acknowledged for equipment support. Valuable suggestions and discussion from Ratchatee Techapiesancharoenkij, Maythee Saisriyoot, and Chatchawal Wongchoosuk are highly appreciated.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tang, H.; Gao, T.; Luo, Z. An electrochemical approach for the determination of the fruit juice freshness using carbon paste electrode modified with ZnO nanorods. *Int. J. Electrochem. Sci.* **2020**, *15*, 2766–2775. [\[CrossRef\]](#)
2. Brima, E.I.; Abbas, A.M. Determination of citric acid in soft drinks, juice drinks and energy drinks using titration. *Int. J. Chem. Stud.* **2014**, *1*, 30–34.
3. Fiume, M.M.; Heldreth, B.A.; Bergfeld, W.F.; Belsito, D.V.; Hill, R.A.; Klaassen, C.D.; Liebler, D.C.; Marks, J.G., Jr.; Shank, R.C.; Slaga, T.J.; et al. Safety assessment of citric Acid, inorganic citrate salts, and alkyl citrate esters as used in cosmetics. *Int. J. Toxicol.* **2014**, *33*, 16S–46S. [\[CrossRef\]](#)
4. Scherer, R.; Rybka, A.C.P.; Ballus, C.A.; Meinhart, A.D.; Filho, J.T.; Godoy, H.T. Validation of HPLC method for simultaneous determination of main organic acid in fruits and juices. *Food Chem.* **2012**, *135*, 150–154. [\[CrossRef\]](#)
5. Izco, J.M.; Tormo, M.; Jiménez-Flores, R. Rapid simultaneous determination of organic acids, free amino acids, and lactose in cheese by capillary electrophoresis. *J. Dairy Sci.* **2002**, *85*, 2122–2129. [\[CrossRef\]](#)
6. Leininger, E.; Katz, S. Fluorometric method for determination of citric acid. *Anal. Chem.* **1949**, *21*, 810–813. [\[CrossRef\]](#)
7. Cen, H.; Bao, Y.; He, Y.; Sun, D.W. Visible and near infrared spectroscopy for rapid detection of citric and tartaric acids in orange juice. *J. Food Eng.* **2007**, *82*, 253–260. [\[CrossRef\]](#)
8. Pucher, G.W.; Sherman, C.C.; Vickery, H.B. A method to determine small amounts of citric acid in biological material. *J. Biol. Chem.* **1936**, *113*, 235–245. [\[CrossRef\]](#)
9. Pashchenko, O.; Shelby, T.; Banerjee, T.; Santra, S. A comparison of optical, electrochemical, magnetic, and colorimetric point-of-care biosensors for infectious disease diagnosis. *ACS Infect. Dis.* **2018**, *4*, 1162–1178. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Detpisuttitham, W.; Phanthong, C.; Ngamchana, S.; Rijiravanich, P.; Surareungchai, W. Electrochemical detection of salicylic acid in pickled fruit/vegetable and juice. *J. Anal. Test.* **2020**, *4*, 291–297. [\[CrossRef\]](#)
11. Sandford, C.; Edwards, M.A.; Klunder, K.J.; Hickey, D.P.; Li, M.; Barman, K.; Sigman, M.S.; White, H.S.; Minter, S.D. A synthetic chemist's guide to electroanalytical tools for studying reaction mechanisms. *Chem. Sci.* **2019**, *10*, 6404–6422. [\[CrossRef\]](#)
12. Pisoschi, A.M.; Danet, A.F.; Kalinowski, S. Ascorbic acid determination in commercial fruit juice samples by cyclic voltammetry. *J. Autom. Methods Manag. Chem.* **2008**, *2008*, 937651. [\[CrossRef\]](#)
13. Ismail, F.A.; Osman, R.A.M.; Idris, M.S.; Hambali, N.A.M.A. Structure and electrical characteristics of BaTiO₃ and Ba_{0.99}Er_{0.01}TiO₃ ceramic. *Solid State Phenom.* **2018**, *280*, 127–133. [\[CrossRef\]](#)
14. Zhao, X.; Liu, W.; Chen, W.; Li, S. Preparation and properties of BaTiO₃ ceramics from the fine ceramic powder. *Ceram. Int.* **2015**, *41*, S111–S116. [\[CrossRef\]](#)
15. Yoon, D.H. Tetragonality of barium titanate powder for a ceramic capacitor application. *J. Ceram. Process. Res.* **2006**, *7*, 343–354.
16. Cai, W.; Fu, C.; Gao, J.; Guo, Q.; Deng, X.; Zhang, C. Preparation and optical properties of barium titanate thin films. *Phys. B* **2011**, *406*, 3583–3587. [\[CrossRef\]](#)
17. Petraru, A.; Schubert, J.; Schmid, M.; Buchal, C. Ferroelectric BaTiO₃ thin-film optical waveguide modulators. *Appl. Phys. Lett.* **2002**, *81*, 1375–1377. [\[CrossRef\]](#)
18. Soderznik, K.Z.; Fabrega, C.; Ramirez, F.H.; Prades, J.D.; Ceh, M. BaTiO₃ based nanostructures for humidity sensing applications. *Proceedings* **2019**, *15*, 9. [\[CrossRef\]](#)
19. Hasbullah, N.N.; Jew, L.O.; Chyi, J.L.Y.; Kien, C.S.; Talib, Z.A. Synthesis of BaTiO₃ nanoparticles via hydrothermal method. *Solid State Phenom.* **2017**, *268*, 172–176. [\[CrossRef\]](#)
20. Simon-Seveyrat, L.S.; Hajjaji, A.; Emziane, Y.; Guiffard, B.; Guyomar, D. Re-investigation of synthesis of BaTiO₃ by conventional solid-state reaction and oxalate coprecipitation route for piezoelectric applications. *Ceram. Int.* **2007**, *33*, 35–40. [\[CrossRef\]](#)
21. Kaviani, R.; Saidi, A. Sol-gel derived BaTiO₃ nanopowders. *J. Alloy. Comp.* **2009**, *468*, 528–532. [\[CrossRef\]](#)
22. Gryteselv, M. Novel Synthesis Method of BaTiO₃-Nanoparticles—Synthesis of BaTiO₃-Nanoparticles by Spray-Pyrolysis of TiO₂-Nanoparticles Dispersed in Ba(NO₃)₂-Solution. Master's Thesis, Norwegian University of Science and Technology (NTNU), Trondheim, Norway, June 2016.
23. Clabel, H.J.L.; Awan, I.T.; Pinto, A.H.; Nogueira, I.C.; Bezzon, V.D.N.; Leite, E.R.; Balogh, D.T.; Mastelaro, V.R.; Ferreira, S.O.; Marega, M., Jr. Insights on the mechanism of solid state reaction between TiO₂ and BaCO₃ to produce BaTiO₃ powders: The role of calcination, milling, and mixing solvent. *Ceram. Int.* **2020**, *46*, 2987–3001. [\[CrossRef\]](#)
24. Ashiri, R. On the solid-state formation of BaTiO₃ nanocrystals from mechanically activated BaCO₃ and TiO₂ powders: Innovative mechanochemical processing, the mechanism involved, and phase and nanostructure evolutions. *RSC Adv.* **2016**, *6*, 17138–17150. [\[CrossRef\]](#)
25. Varshney, G.; Kanel, S.R.; Kempisty, D.; Varshney, V.; Agrawal, A.; Sahle-Demessie, E.; Varma, R.S.; Nadagouda, M.N. Nanoscale TiO₂ films and their application in remediation of organic pollutants. *Coord. Chem. Rev.* **2016**, *1*, 43–64. [\[CrossRef\]](#)
26. Movlee, K.; Ganjali, M.R.; Norouzi, P.; Neri, G. Iron-based nanomaterials/graphene composites for advanced electrochemical sensor. *Nanomaterials* **2017**, *7*, 406. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Khort, A.A.; Podbolotov, K.B. Preparation of BaTiO₃ nanopowders by the solution combustion method. *Ceram. Int.* **2016**, *42*, 15343–15348. [\[CrossRef\]](#)
28. Jongprateep, O.; Tanmee, K. Effect of fuel concentrations and calcination temperature on the particle sizes of YBa₂Cu₃O_{7-x} superconductors synthesized by the solution combustion technique. *J. Austr. Ceram. Soc.* **2012**, *48*, 80–84.

29. Hwang, H.S.; Jeong, J.W.; Kim, Y.A.; Chang, M. Carbon nanomaterials as versatile platforms for biosensing applications. *Micromachines* **2020**, *11*, 814. [\[CrossRef\]](#)
30. Bai, W.; Raghavendra, A.; Podila, R.; Brown, J.M. Defect density in multiwalled carbon nanotubes influences ovalbumin adsorption and promotes macrophage activation and CD4+ T-cell proliferation. *Int. J. Nanomed.* **2016**, *11*, 4357–4371.
31. Wang, C.; Yang, F.; Gao, L.; Xu, S.; Fan, L.; Guo, T.; Liu, Y.; Zhou, L.; Zhang, Y. AuPt nanoparticles clusters on MWCNTs with enhanced electrocatalytic activity for methanol oxidation. *Catalysts* **2018**, *8*, 669. [\[CrossRef\]](#)
32. Kwon, W.; Kim, J.M.; Rhee, S.W. Electrocatalytic carbonaceous materials for counter electrodes in dye-sensitized solar cells. *J. Mater. Chem. A* **2013**, *1*, 3202–3215. [\[CrossRef\]](#)
33. Yusoff, F.; Mohamed, N.; Aziz, A.; Ghani, S.A. Electrocatalytic reduction of oxygen at perovskite (BSCF)-MWCNT composite electrodes. *Mater. Sci. Appl.* **2014**, *5*, 199–211. [\[CrossRef\]](#)
34. Muthumariyappan, A.; Rajaji, U.; Chen, S.M.; Baskaran, N.; Chen, T.W.; Jothi Ramalingam, R.J. Sonochemical synthesis of perovskite-type barium titanate nanoparticles decorated on reduced graphene oxide nanosheets as an effective electrode material for the rapid determination of ractopamine in meat samples. *Ultrason. Sonochem.* **2019**, *56*, 318–326. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Vittayakorn, N. Synthesis and dielectric properties of bismuth doped barium titanate (BaTiO₃) ceramics. *NU Sci. J.* **2007**, *3*, 119–125.
36. Ma, Z.; Li, G.; Sun, B.; He, L.; Gao, W.; Sun, Q.; Liu, Q.; Lou, X. Enhanced electric-field-induced strain in 0.7Bi_(1-x)Sm_xFeO₃-0.3BaTiO₃ lead-free ceramics. *J. Mater. Sci.* **2020**, *55*, 8134–8144. [\[CrossRef\]](#)
37. Mansuri, A.; Mishra, A. Structure evolution of BaTiO₃ on Co doping: X-ray diffraction and raman study. *J. Phys. Conf. Ser.* **2016**, *755*, 012018. [\[CrossRef\]](#)
38. Thanki, A.A.; Goyal, R.K. Study on effect of cubic- and tetragonal phased BaTiO₃ on the electrical and thermal properties of polymeric nanocomposites. *Mater. Chem. Phys.* **2016**, *183*, 447–456. [\[CrossRef\]](#)
39. Petrovic, M.M.V.; Radojkovic, A.; Bobic, J.D.; Dzunuzovic, A.; Ilic, N.; Stojanovic, B.D. Sensing properties of barium titanate nanoceramics tailored by doping and microstructure control. *J. Mater. Sci.* **2019**, *54*, 6038–6052. [\[CrossRef\]](#)
40. Chaudhari, G.N.; Bambole, D.R.; Bodade, A.B. Structural and gas sensing behavior of nanocrystalline BaTiO₃ based liquid petroleum gas sensors. *Vacuum* **2006**, *81*, 251–256. [\[CrossRef\]](#)
41. Jongprateep, O.; Khondnakhon, T.; Palomas, J. Composition-microstructure-property relationships in BaTiO₃ with Mg addition. *Key Eng. Mater.* **2015**, *659*, 58–63. [\[CrossRef\]](#)
42. Hong, T.; Brinkman, K.S.; Xia, C. Barium carbonate nanoparticles as Synergistic catalysts for the oxygen reduction reaction on La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Solid-oxide fuel cell cathodes. *ChemElectroChem* **2016**, *3*, 805–813. [\[CrossRef\]](#)
43. Cao, E.; Feng, Y.; Guo, Z.; Wang, H.; Song, G.; Zhang, Y.; Hao, W.; Sun, L.; Nie, Z. Ethanol sensing characteristics of (La,Ba)(Fe,Ti)O₃ nanoparticles with impurity phases of BaTiO₃ and BaCO₃. *J. Sol-Gel Sci. Technol.* **2020**, *96*, 431–440. [\[CrossRef\]](#)
44. Li, B.; Shang, W.; Hu, Z.; Zhang, N. Template-free fabrication of pure single-crystalline BaTiO₃ nano-wires by molten salt synthesis technique. *Ceram. Int.* **2014**, *40*, 73–80. [\[CrossRef\]](#)
45. Su, S.; Zuo, R.; Lv, D.; Fu, J. Synthesis and characterization of (001) oriented BaTiO₃ platelets through a topochemical conversion. *Powder Technol.* **2012**, *217*, 11–15. [\[CrossRef\]](#)
46. Dutta, P.D.; Roy, M.; Maiti, N.; Tyagi, A.K. Phase evolution in sonochemically synthesized Fe³⁺ doped BaTiO₃ nanocrystallites: Structural, magnetic and ferroelectric characterisation. *Phys. Chem. Chem. Phys.* **2016**, *18*, 9758–9769. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Gao, Y.; Ma, J.; Meng, F.; Wang, W.; Li, Z. Solution-combusted nanosized Ni-Al₂O₃ catalyst for slurry CO methanation: Effects of alkali/alkaline earth metal chlorides. *J. Mater. Sci.* **2020**, *55*, 16510–16521. [\[CrossRef\]](#)
48. Khort, A.; Podbolotov, K.; Serrano-Garcia, R.; Gun'ko, Y. One-step solution combustion synthesis of pure Ni nanopowders with enhanced coercivity: The fuel effect. *J. Solid State Chem.* **2017**, *253*, 270–276. [\[CrossRef\]](#)
49. Kim, D.; Zhang, K.; Cho, M.; Kang, Y.M. Critical design factors for kinetically favorable P-based compounds toward alloying with Na ions for high-power sodium-ion batteries. *Energy Environ. Sci.* **2019**, *12*, 1326–1333. [\[CrossRef\]](#)
50. Sato, Y.; Kitano, S.; Kowalski, D.; Aoki, Y.; Fujiwara, N.; Ioroi, T.; Habazaki, H. Spinel-type metal oxide nanoparticles supported on platelet-type carbon nanofibers as a bifunctional catalyst for oxygen evolution reaction and oxygen reduction reaction. *Electrochemistry* **2020**, *88*, 566–573. [\[CrossRef\]](#)
51. Liu, Y.; Zhang, J.; Cheng, Y.; Jiang, S.P. Effect of carbon nanotubes on direct electron transfer and electrocatalytic activity of immobilized glucose oxidase. *ACS Omega* **2018**, *3*, 667–676. [\[CrossRef\]](#)
52. Ferrara, M.; Melchionna, M.; Fornasiero, P.; Bevilacqua, M. The role of structured carbon in downsized transition metal-based electrocatalysts toward a green nitrogen fixation. *Catalysts* **2021**, *11*, 1529. [\[CrossRef\]](#)
53. Dey, S.; Dhal, G.C.; Mohan, D.; Prasad, R. Advances in transition metal oxide catalysts for carbon monoxide oxidation: A review. *Adv. Compos. Hybrid Mater.* **2019**, *2*, 626–656. [\[CrossRef\]](#)
54. Poolakkandy, R.R.; Menamparambath, M.M. Transition metal oxide based non-enzymatic electrochemical sensors: An arising approach for the meticulous detection of neurotransmitter biomarkers. *Electrochem. Sci. Adv.* **2021**, *1*, e2000024. [\[CrossRef\]](#)
55. Fayemi, O.E.; Adekunle, A.S.; Ebenso, E.E. Metal oxide nanoparticles/multi-walled carbon nanotube nanocomposite modified electrode for the detection of dopamine: Comparative electrochemical study. *J. Biosens. Bioelectron.* **2015**, *6*, 1000190. [\[CrossRef\]](#)
56. Kim, M.J.; Choe, S.; Kim, H.C.; Cho, S.K.; Kim, S.K.; Kim, J.J. Electrochemical behavior of citric acid and its influence on Cu electrodeposition for damascene metallization. *J. Electrochem. Soc.* **2015**, *162*, D354–D359. [\[CrossRef\]](#)

57. Fotouhi, L.; Fathollahzadeh, M.; Heravi, M.M. Electrochemical behavior and voltametric determination of sulfaguanidine at a glassy carbon electrode modified with a multi-walled carbon nanotube. *Int. J. Electrochem. Sci.* **2012**, *7*, 3919–3928.
58. Wu, Y.; Deng, P.; Tian, Y.; Feng, J.; Xiao, J.; Li, J.; Liu, J.; Li, G.; He, Q. Simultaneous and sensitive determination of ascorbic acid, dopamine and uric acid via an electrochemical sensor based on PVP-graphene composite. *J. Nanobiotechnol.* **2020**, *18*, 112. [\[CrossRef\]](#)
59. Maddipatla, D.; Saeed, T.S.; Narakathu, B.B.; Obare, S.O.; Atashbar, M.Z. Incorporating a novel hexaazatriphenylene derivative to a flexible screen-printed electrochemical sensor for copper ion detection in water samples. *IEEE Sens. J.* **2020**, *20*, 12582–12591. [\[CrossRef\]](#)
60. Saavedra, L.; García, A.; Barbas, C. Development and validation of a capillary electrophoresis method for direct measurement of isocitric, citric, tartaric and malic acids as adulteration markers in orange juice. *J. Chromatogr. A* **2000**, *881*, 395–401. [\[CrossRef\]](#)
61. López, E.F.; Gómez, E.F. Simultaneous determination of the major organic acids, sugars, glycerol, and ethanol by HPLC in grape musts and white wines. *J. Chromatogr. Sci.* **1996**, *34*, 254–257. [\[CrossRef\]](#)
62. Cunha, S.C.; Ferreira, I.M.P.L.V.O.; Fernandes, J.O.; Faria, M.A.; Beatriz, M.; Oliveira, P.P.; Ferreira, M.A. Determination of lactic, acetic, succinic, and citric acids in table olives by HPLC/UV. *J. Liq. Chrom. Relat.* **2001**, *24*, 1029–1038. [\[CrossRef\]](#)
63. Zhang, Y.; Zhao, Y.; Zhou, A.; Qu, Q.; Zhang, X.; Song, B.; Liu, K.; Xiong, R.; Huang, C. “Turn-on” ratiometric fluorescent probe: Naked-eye detection of acidic pH and citric acid (CA) by using fluorescence spectrum and its application in real food samples and zebrafish. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2021**, *261*, 120014. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Terazawa, K.; Takatori, T. An enzymic colorimetry of citric acid with pyruvate oxidase. *Jpn. J. Clin. Chem.* **1984**, *13*, 53–57.
65. Do Nascimento, R.F.; Selva, T.M.G.; Ribeiro, W.F.; Belian, M.F.; Angnes, L.; do Nascimento, V.B. Flow-injection electrochemical determination of citric acid using a cobalt(II)-phthalocyanine modified carbon paste electrode. *Talanta* **2013**, *105*, 354–359. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Awasthi, S.; Srivastava, A.; Singla, M.L. Voltammetric determination of citric acid and quinine hydrochloride using polypyrrole-pentacyanonitrosylferrate/platinum electrode. *Synth. Met.* **2011**, *161*, 1707–1712. [\[CrossRef\]](#)
67. Selvam, S.P.; Chinnadaiyala, S.R.; Cho, S.; Yun, K. Differential pulse voltametric electrochemical sensor for the detection of etidronic acid in pharmaceutical samples by using rGO-Ag@SiO₂/Au PCB. *J. Nanomater.* **2020**, *10*, 1368. [\[CrossRef\]](#) [\[PubMed\]](#)
68. Keerthi, M.; Boopathy, G.; Chen, S.M.; Chen, T.W.; Rwei, S.P.; Liu, X. An efficient electrochemical sensor based on Ag nanoparticle decorated MnO₂/reduced graphene oxide ternary nanocomposite for detection of acetaminophen in human urine sample. *Int. J. Electrochem. Sci.* **2019**, *14*, 346–358. [\[CrossRef\]](#)
69. Pecharsky, V.K.; Zavalij, P.Y. *Fundamentals of Powder Diffraction and Structural Characterization of Materials*, 1st ed.; Springer: New York, NY, USA, 2005; pp. 384–388.
70. Jongprateep, O.; Palomas, J. Effects of Mg addition and sintering temperatures on chemical compositions, microstructures, densities and dielectric properties of strontium titanate. *Ceram. Int.* **2015**, *41*, S63–S68. [\[CrossRef\]](#)