Article

Fabrication of Polyaniline Ni-Complex Catalytic Electrode by Plasma Deposition for Electrochemical Detection of Phosphate through Glucose Redox Reaction as Mediator

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Abstract: We report here the preparation and characterization of polyaniline Ni-complex catalytic electrode by one-pot plasma deposition for the electrochemical detection of phosphate via the redox reaction of glucose. We first prepared a precursory solution by combining NiCl₂ and 3-aminobenzoic acid in a mixed solution of methanol (MeOH) and water, and adding aniline as a conductive polymeric precursor for increasing the electron transfer potential. We then synthesized the catalytic electrode in a one-step cold plasma process by preparing the precursors on ITO glass. We characterized the obtained Ni-coordinate catalytic electrode via X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (SEM), and electrochemical methods. Electrochemical characterization produced stable redox properties of Ni³⁺/Ni²⁺ couples in a 0.1 M NaOH solution. Cyclic voltametric experiments have drastically increased electrocatalytic oxidation and reduction of glucose by increasing the concentration of phosphate (PO₄³⁻) ions using the prepared Ni-modified catalytic electrodes. From these results, the prepared catalytic electrode could be used as the electrochemical sensor for phosphate in actual water.

Keywords: plasma deposition; polyaniline Ni-complex catalytic electrode; electrochemical detection; phosphate ion; glucose; redox behavior of Ni³⁺/Ni²⁺ couples

1. Introduction

Quantitative evaluation of phosphates, both of inorganic compounds and organic compounds, is important in biomedical research, biological diagnosis, and environmental monitoring [1–3]. The sensing range of phosphorus is between 0.2 in 10 mg/L in natural and waste waters and between 0.2 and 50 mg/kg in soil. A maximum permissible concentration of phosphate in river water is 0.32 µM and ranges between 0.0143 and 0.143 mM in wastewater [4]. As a diagnostic fluid, the concentration of phosphate ions in human saliva is variable, ranging from between 5 and 14 mM [5]. Adult human serum with a range of 0.81 to 1.45 mM PO₄³⁻ was used [6]. Many researchers have developed various detection methods for phosphate such as phosphate ion selective electrodes [7], chromatography [8], spectroscopy [9], and the development of sensors exploiting enzymatic reactions [10,11]. However, little has been reported about electrochemical detection, which is known as a simpler method than those described above.

On the other hand, there are many studies published about the nonenzymatic electrochemical detection of glucose based on metallic nanoparticle electrodes, which contain Ni, Pd, Au, Co, and nanoparticles, etc. [12,13]. Furthermore, metal-complex electrodes were also reported such as Cu-complex, Ni-complex, and Zn-complex electrode, etc., for the detection of glucose [14,15]. In a previous paper, we also prepared the Ni-complex electrode by a plasma process for the detection of methanol [16]. In the study, we used polyacrylic acid as ligands to immobilize the metal Ni. However, though polyacrylic acid...
was a good ligand for immobilizing Ni ions, the vinyl polymers and polyacrylic acid were not good electron transfer materials because of their low conductivity.

Conducting polymers are important functional materials which have been widely applied to prepare electrochemical biosensors, due to their interesting and tunable chemical, electrical, and structural properties [17–20]. Therefore, conducting polymers have been widely applied in the fields of bioanalytical and biomedical science [21], drug delivery [22,23], tissue engineering [24], and cell culture [25] because of their essential properties and biocompatibility [26,27]. In addition, conducting polymers express an attractive sensitive material for biosensors because of electrical properties that allow them to transmit biochemical information onto electrical signals. Furthermore, conducting polymers can be easily grafted by modifying their functional groups, which offers the possibility of improving their ability to sense and quantify bioanalytes or to maximize the interactions between biomolecules and functional polymers [28,29]. Therefore, after a short explanation of the electrochemical processes used in conducting polymer-based biosensors, the biosensors will be described to enhance the recently advanced research into conducting polymer-based electrochemical biosensors.

Low temperature plasmas can be prepared for polymers in laboratories and in industrial applications. Low temperature plasma is the electric glow discharge made by using power sources such as AC, DC, and microwave [30–32]. Alternatively, high temperature plasmas are not used for making organic materials due to their heat labile characteristics. Plasma polymerization is not limited to preparing organic materials, and the plasma synthesis of inorganic materials should be included in plasma polymerization. However, little has been reported about the plasma polymerization of aniline as a conducting polymer precursor because it was difficult to make conjugation bonds from the main chains in polyaniline by plasma polymerization until now.

In this study, we first fabricated polyaniline Ni-coordinate catalytic electrode by applying a one-step plasma polymerization process and investigated the electrochemical redox of glucose as a mediator to measure the phosphate ion for the electrochemical sensor of phosphate in actual water. We found that a polyaniline Ni-complex catalytic electrode can be applied as an electrochemical oxidation for glucose in the presence of high concentrations of phosphate.

2. Results
2.1. Contact Angle Analysis

The No. 1, 2, 3, and 4 electrodes used were: an indium tin oxide (ITO) electrode; a polyaniline-grafted ITO electrode; the benzoic acid-modified polyaniline electrode; and a polyaniline Ni-complex catalytic electrode, respectively. Figure 1 shows the contact angles of the prepared polyaniline Ni-coordinate catalytic electrodes found by applying the plasma process. The contact angle is important wherever the intensity of the phase contact between liquid and solid substances needs to be checked or assessed. By examining the water contact angles, we determined that the contact angle of the bare ITO electrode, No. 1 was 77° and the contact angles of the polyaniline Ni-coordinated catalytic electrodes, No. 2, No. 3, and No. 4 were 60°, 53°, and 51°, respectively, at room temperature. As a result, the base ITO glass had nearly hydrophobic characteristics and a high contact angle. Compared to base ITO glass, the contact angles of the prepared polyaniline Ni-coordinated electrodes were remarkably low, due to the presence of a large amount of the functionalized COOH groups from 3-aminobenzoic acid, which had hydrophilic properties. The existence of hydrophilic metallic coordination materials on each electrode also converted hydrophobic ITO to hydrophilic characteristics. From these results, we concluded that the polymeric metallic (Ni)-complex surface has hydrophilic properties. It is shown that the polyaniline Ni-complex catalytic electrode was successfully coated onto ITO surfaces by the one-pot plasma process easily and simply.
The surface morphologies of the original ITO electrode (No. 1) and the polyaniline Ni-complex catalytic electrodes (No. 2, 3, and 4 in Table 1), were exhibited by scanning them with electron microscopy (SEM) (Figure 2). The polyaniline Ni-complex catalytic electrode surface appears amorphous, morphology that was suggested by the clear deposition of polyaniline Ni-complex onto the ITO substrate. When we used a cross-linker of 3-aminobenzoic acid (No. 3 and 4), the polyaniline was aggregated because the main chains of polyaniline connected with each other.

Figure 2. SEM images of the prepared catalytic electrode surface by plasma deposition (see Table 1).

2.3. AFM Data Analysis

Figure 3 exhibits the AFM data of the prepared polyaniline Ni-complex catalytic electrode surfaces by the one-pot plasma process (see Table 1). In No. 1, the ITO surface roughness is lower than that of the polyaniline-grafted ITO electrode (No. 2), the benzoic acid-modified polyaniline electrode (No. 3), and the polyaniline Ni-complex catalytic electrode (No. 4). These results mean that the polyaniline Ni-complex catalytic electrodes were successfully coated by one-pot cold plasma deposition.
2.4. EDS Data Analysis

Figure 4 demonstrates SEM-EDAX analysis of the prepared polyaniline Ni-complex catalytic electrode surfaces by cold plasma deposition (No. 4 in Table 1). The EDAX images of the prepared Ni-complex catalytic electrodes exhibit significant spots of carbon, oxygen, and Ni on their surfaces. This means that the surface deposition of polyaniline Ni-complex on the ITO electrodes via the one-step cold plasma process was successful.

2.5. XPS Data Analysis

Figure 5 shows the XPS survey scan spectra data of the amino benzoic acid-modified polyaniline (No. 3) and the polyaniline Ni-complex catalytic electrodes (No. 4) fabricated via cold plasma deposition. In No. 3, there are no Ni peaks at 853 eV, while in No. 4, the two peaks at 853.3 eV and 834.9 eV, included binding to the energies of NiO 2p^{3/2} and NiO 2p^{1/2}, designating the presence of Ni in the electrode. Additionally, the peaks at 400 eV suggest that the N is in the form of cross-linked chemicals of amino benzoic acid, acting as ligands. The O1s peak is roughly 531.8 eV, which indicates the presence of a carboxylic acid (amino benzoic acid) in the electrode.
The cyclic voltammogram of the synthesized Ni-complex catalytic electrodes facilitated phosphate in NaOH electrolytes with glucose and Ni-complex catalytic electrodes to obtain prepared polyaniline Ni-complex catalytic electrodes. Figure 6 exhibits the cyclic voltammogram (see Table 1).

2.6. Electrochemical Data Analysis

We performed cyclic voltammetry to determine the electrochemical performance of the prepared polyaniline Ni-complex catalytic electrodes. Figure 6 exhibits the cyclic voltammetry (CV) of these electrodes in 0.1 M NaOH electrolyte with a scan rate of 100 mV/min. The cyclic voltammogram of the synthesized Ni-complex catalytic electrodes facilitated the oxidation-reduction peak, which was indicated by the oxidation and reduction of the Ni$^{2+}$/Ni$^{3+}$ couple in the NaOH electrolyte on the left side. From these results, we suggest that the Ni-complex catalytic electrode could be used as an electrochemical catalyst sensor for the detection of organic molecules. Therefore, we selected glucose as the mediator molecule to obtain its redox peak. When we added the glucose to NaOH electrolytes, the redox peaks of Ni$^{2+}$/Ni$^{3+}$ couples of the polyaniline Ni-complex catalytic electrode were shifted as shown by the red line of cyclic voltammogram on the right side in Figure 6. Furthermore, the current values and electrochemical potential windows were increased by adding glucose. These results mean the glucose is also oxidized and reduced on the Ni-complex catalytic electrode. To determine phosphate ion molecules, we added sodium phosphate in NaOH electrolytes with glucose and Ni-complex catalytic electrodes to obtain the shifted redox peaks of cyclic voltammograms, as shown by the blue line on the right side in Figure 6. These results strongly indicate that the prepared Ni-complex catalytic electrode could be used as an electrochemical catalytic sensor for the detection of phosphate.
The current value of the fabricated Ni-complex catalytic electrode decreased to about 21.3% from its maximum peak after 120 cycles, which suggests an acceptable stability was achieved.

2.7. Electrochemical Detection of Phosphate

Figure 7 shows cyclic voltammograms of 1.0 mM glucose by the prepared Ni-complex catalytic electrode (No. 4) in 0.1 M NaOH electrolytes with different sodium phosphate levels and a scan rate of 100 mV/min. The redox peaks of glucose rose by increasing the concentration of sodium phosphate to 0.006 M. This electrochemical detection indicated that the prepared Ni-complex catalytic electrode could be used as an electrocatalytic biosensor for sensing phosphate ions. The catalytic efficiency, presented as a current density value of the fabricated Ni-complex catalytic electrodes for detection of glucose oxidation without sodium phosphate, was calculated to be 11.5 mAM−1 cm−2. We also examined that the stability of the fabricated polyaniline Ni-complex catalytic electrode via cyclic voltammetry. The current value of the fabricated Ni-complex catalytic electrode decreased to about 21.3% from its maximum peak after 120 cycles, which suggests an acceptable stability was achieved.

3. Discussion

The polymeric metal coordination of chemicals with Ni2+/Ni3+ redox couples have received considerable interest in recent years due to their properties of alkalinizing electrolytes. There are many common applications for using redox mediators between target compounds and the prepared electrodes in many electrochemical redox processes. Furthermore, the fabrication process is usually simple and easy and the characteristics of the coatings that result can be carefully controlled [33]. In a previous paper [16,34], polymeric metal complex chemicals with Ni, Cu, and Fe were synthesized via an alternate current
(AC) plasma deposition process to detect H$_2$O$_2$ and methanol, respectively. The exhibited method of polymeric fabrication, specifically, conducting a polymer metallic coordinator with a glucose redox reaction as a catalytic mediator, was effective. Therefore, we examined the plasma polymerization of the precursors as shown in Figure 8. Figure 8 exhibits the schematic preparation of polyaniline Ni-complex catalytic electrode by plasma process for detection of phosphate. If we begin with aniline as an electron transfer material, metal salts as catalytic mediators can be synthesized by coordinating metal ions with the carboxyl groups of 3-aminobenzoic acid.

![Figure 8. Schematic preparation of polyaniline Ni-complex catalytic electrode by plasma process for detection of phosphate.](image)

On the other hand, linear polyaniline can be synthesized in two ways: by chemical oxidation of aniline monomers in an acid solution [35]; or by electrochemical oxidation [36]. Cross-linked polyaniline exhibits characteristics similar to that of linear polyaniline but with lower values of conductivity and solubility in solvents and a higher mechanical strength [37]. Plasma polymerization is a more easy and simple process than conventional polymerization, which involves casting film from a solution because the fewer fabrication steps are needed in the former. It is a free solvent, room temperature process that does not require the use of chemical oxidants. The ultra-thin film with controllable thicknesses in the nanometer range can easily be formed on the surfaces of substrates by plasma polymerization [38]. Plasma polymerization mechanisms are a major source of free radicals and negative ions attributed to the collisions of the monomer molecules with electrons generated by electric discharges [39]. The polymers from plasma polymerization do not contain regularly repeating units; while the chains are branched and randomly terminated with a high degree of cross-linking. The free radicals are trapped, and this results in changes to the plasma polymer network over time [40]. Polyaniline formations on film structures by plasma polymerization have been reported earlier. There is not much detailed information available about polyaniline structure by plasma polymerization.

In our case, plasma is a partially ionized gas with radicals, ions, electrons, photons, and molecules that are excited during the plasma process. It is a highly reactive mixture of species, which are different from conventional gaseous mixtures. The resulting catalysts under the influence of plasma, can include very different species from those prepared by conventional thermal preparation. Plasma has been extensively applied for catalyst preparation because of this [16]. In this experiment, the precursors with metallic coordination were vaporized as plasma. Polymeric-Ni coordinated chemicals with special morphology were controlled through a fast-collision process using a quenched gas, as shown in Figure 9. Figure 9 shows the possible polymerization mechanism of the functional polyaniline during the cold plasma process. During the plasma process, precursor radicals were generated as shown in Figure 9 (1), and then the generated aniline radicals were polymerized as shown by the schematic in Figure 9 (2) and (3). Finally, we obtained the carboxylic acid-modified polyaniline as shown in Figure 9 (4).
Figure 9. Possible polymerization mechanism of the functional polyaniline during cold plasma process.

Figure 10 exhibits the electrocatalytic mechanism of a glucose redox reaction on the surface of a Ni-complex polymeric catalytic electrode. The Ni\(^{2+}\) was first electrochemically oxidized to Ni\(^{3+}\), which then reacted electrochemically with glucose and resulted in the glucose converting to products such as lactone and in the regeneration of the catalyst.

Figure 10. Catalytic redox mechanism of glucose on polyaniline Ni-complex electrode prepared by plasma process for detection of phosphate.

Figure 11 exhibits the formation of D-(+)-glucos-6-phosphate during the electrochemical process of alkaline electrolytes with the presence of a phosphate ion. The prepared D-glucose-6-phosphate compounds show the shifted redox peaks as shown in Figure 11.
4. Materials and Methods

4.1. Reagents

Aniline, indium tin oxide (ITO) plate as the working electrode (30–60 Ω/sq, 25 mm × 25 mm × 1.1 mm, Sigma Aldrich Co.), 3-Aminobenzocic Acid (Tokyo Kasei), nickel chloride (NiCl2, Oriental Chemical Industry, Osaka, Japan), potassium chloride (KCl, Ducsan Pharmaceutical Co., Ltd., Seoul, Korea), methyl alcohol (MeOH, Samchun, Pyeongtaek-si, Korea), and sodium hydroxide (NaCl, Samchun) were purchased, respectively, and used during treatments.

Phosphate buffer solution (PBS) was synthesized by mixing 0.1 M NaH2PO4 and 0.1 M Na2HPO4 and the pH was controlled to a value of 7.4. For this, we obtained a water purification experiment solution by Milli Q plus water purification systems (Millipore, Co., Ltd., Toronto, ON, Canada), and the final resistance of water was 18.2 MΩ cm−1.

4.2. Research Instruments

We determined the surface characteristics and contact angle (PHOENIX 300, Surface Electro Optics Co., Ltd., Seoul, Korea), using scanning electron microscopy (FE-SEM, S 4800, Hitachi, Tokyo, Japan) and X-ray photoelectron spectroscopy (MultiLab. ESCA 2000, Thermo Fisher Scientific, Inc., MA, USA). We performed cyclic voltammetry (CV) using a VersaSTAT 3 potentiostat/galvanostat (AMETEK, Pennsylvania, USA) and a conventional 3 electrode system with an ITO plate as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as a reference electrode.

We used a plasma device with power restricted to the range of 200 to 250 W. The torch used in this experiment was conical and the diameter of the torch tip was 2.0 mm. Nitrogen was supplied as the working gas in a tank connected to the plasma generator, with a flow controller inside. The plasma generator was applied to hold the pressure at a constant level. The percussor solution was injected into the plasma device jet by a syringe pump in the downstream region. The ITO plate was placed under a plasma jet at a distance of 1 cm and manually moved during the plasma deposition process.

4.3. Preparation of Polyaniline Ni-Complex Catalytic Electrode

Table 1 exhibits the preparation condition of precursors for AC plasma process. We prepared the precursor solutions for the experiment as follows. First, a precise amount of a nickel chloride salt was dissolved in the mixture of a water and methanol solution, and then added the 3-aminobenzoic acid as ligands and aniline as the electron transfer material. This detailed the precursor solution for the preparation of polyaniline Ni-complex catalytic electrode as shown in Table 1. Subsequently, the ITO plate was pre-washed in ethanol and ultrasonicated for ten minutes before plasma deposition. The ITO substrate was slowly moved in the x and y directions during the deposition process and the deposition time was 5 min. The precursors were injected into the AC plasma jet using a syringe pump at a flow rate of 0.3 mL/min, and the nitrogen gas pressure was kept constant at 0.018 MPa. After the deposition process was completed, the prepared electrode was washed in a MeOH/H2O mixture to remove nonreactive precursors, then dried and stored at 4 °C before application.
Table 1. Preparation condition of precursors for AC plasma process.

| No.  | Aniline (mmol) | 3-Aminobenzocic Acid (mmol) | Nickel Chloride (mmol) | Water (mL) | MeOH (mL) |
|------|----------------|-----------------------------|------------------------|------------|-----------|
| No. 1 | -              | -                           | -                      | -          | -         |
| No. 2 | 54.8           | -                           | -                      | -          | -         |
| No. 3 | 54.8           | 0.2                         | 0.2                    | 0.5        | 0.08      |
| No. 4 | 54.8           | 0.2                         | 0.2                    | 0.5        | 0.04      |

5. Conclusions

The polyaniline Ni-coordinate catalytic electrode for glucose oxidation could be successfully prepared by a one-pot plasma process of synthesized precursor solutions. We successfully fixed the fabricated Ni-complex catalytic electrode with Ni coordination chemicals on the surface of an ITO substrate by adjusting SEM, contact angle, XPS, cyclic voltammetry, and SEM-EDS, and evaluated the catalytic efficiency of glucose in an alkaline solution. From the results, we have arrived the following conclusions:

1. A polyaniline Ni-coordinated catalytic electrode can be fabricated easily and simply by one-pot plasma deposition without further treatment.
2. The catalytic activity and anodic peak potential of glucose were 11.5 mAM$^{-1}$cm$^{-2}$ and 0.54 V, respectively. Therefore, the polyaniline Ni-complex catalytic electrode shows higher catalytic activity for glucose oxidation.
3. By adding phosphate, the currents of anodic peak potential rose as phosphate ion concentration increased.
4. The stability of the polymeric Ni coordination electrode seems to be acceptable for practical applications.
5. The fabricated polyaniline Ni-complex catalytic electrode could be used as phosphate sensors.

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References

1. Min, J.-K.; Yoo, H.-S.; Lee, E.-Y.; Lee, W.-J.; Lee, Y.-M. Simultaneous Quantitative Analysis of Sphingoid Base 1-Phosphates in Biological Samples by o-Phthalaldehyde Pre-column Derivatization after Dephosphorylation with Alkaline Phosphatase. *Anal. Biochem.* 2002, 303, 167–175. [CrossRef]
2. Bian, X.; Li, X.; Qi, P.; Chi, Z.; Ye, R.; Lu, S.; Cai, Y. Quantitative design and analysis of marine environmental monitoring networks in coastal waters of China. *Mar. Pollut. Bull.* 2019, 143, 144–151. [CrossRef]
3. Rouser, G.; Siakotos, A.N.; Fleischer, S. Quantitative analysis of phospholipids by thin-layer chromatography and phosphorus analysis of spots. *Lipids 1966*, 1, 85–86. [CrossRef] [PubMed]
4. Litke, D.W. Review of Phosphorus Control Measures in the United States and Their Effects on Water Quality. In *Water-Investigations Report, USGS*; US Department of the Interior: Washington, DC, USA, 1999; Volume 99.
5. Poureslami, H.; Hoseinifar, R.; Khazaeli, P.; Hoseinifar, R.; Sharifi, H.; Poureslami, P. Changes in the Concentration of Ions in Saliva and Dental Plaque after Application of CPP-ACP with and without Fluoride among 6–9 Year Old Children. *J. Dent. Biomater.* 2017, 4, 361–366.
6. Bansal, V.K. Chapter 198Serum Inorganic Phosphorus. In *Clinical Methods: The History, Physical, and Laboratory Examinations*, 3rd ed.; Butterworths: Boston, MA, USA, 1990.
7. Khaleda, E.; Hassana, H.N.A.; Girgis, A.; Metelka, R. Construction of novel simple phosphate screen-printed and carbon paste ion-selective electrodes. *Talanta 2008*, 77, 737–743. [CrossRef]
8. Kelani, K.M.; Badran, O.M.; Rezk, M.R.; Elghobashy, M.R.; Eid, S.M. Widening the applications of the Just-Dip-It approach: A solid contact screen-printed ion-selective electrode for the real-time assessment of pharmaceutical dissolution testing in comparison to off-line HPLC analysis. *RSC Adv.* 2021, 11, 31855–31864. [CrossRef]

9. Altura, B.M.; Altura, B.T. Role of Magnesium and Calcium in Alcohol-Induced Hypertension and Strokes as Probed by In Vivo Television Microscopy, Digital Image Microscopy, Optical Spectroscopy, 31P-NMR, Spectroscopy and a Unique Magnesium Ion-Selective Electrode. *Alcohol. Clin. Exp. Res.* 1994, 18, 1057–1068. [CrossRef]

10. Law, A.T.; Adelouj, S.B. Progress and recent advances in phosphate sensors: A review. *Talanta* 2013, 114, 191–203. [CrossRef] [PubMed]

11. Zeitoun, R.; Biswas, A. Potentiometric Determination of Phosphate Using Cobalt: A Review. *J. Electrochem. Soc.* 2020, 167, 127507. [CrossRef] [PubMed]

12. Nie, H.; Yao, Z.; Zhou, X.; Yang, Z.; Huang, S. Nonenzymatic electrochemical detection of glucose using well-distributed nickel nanoparticles on straight multi-walled carbon nanotubes. *Biosens. Bioelectron.* 2011, 30, 28–34. [CrossRef] [PubMed]

13. Meng, L.; Jin, J.; Yang, G.; Lu, T.; Zhang, H.; Cai, C. Nonenzymatic Electrochemical Detection of Glucose Based on Palladium–Single-Walled Carbon Nanotube Hybrid Nanostructures. *Anal. Chem.* 2009, 81, 7271–7280. [CrossRef]

14. Benjamini, M.; Manoj, D.; Thenmozhi, K.; Bhagat, P.R.; Saravanakumar, D.; Senthilkumar, S. A bioinspired ionic liquid tagged cobalt-salen complex for nonenzymatic detection of glucose. *Biosens. Bioelectron.* 2017, 91, 380–387. [CrossRef]

15. Yhoub, Z.; Brinda, K.N.; Achar, G.; Malecki, J.G.; Keri, R.S.; Nagaraju, D.H.; Budagumpi, S. Glucose electrocatalysts derived from mono- or dicarbene coordinated nickel(II) complexes and their mesoporous carbon composites. *Appl. Organomet. Chem.* 2021, 35, e6446. [CrossRef]

16. Jeon, J.S.; Yu, I.K.; Kim, W.; Choi, S.-H. Electrocatalytic Oxidation of Methanol by a Polymeric Ni Complex-modified Electrode Prepared by a One-step Cold-Plasma Process. *Front. Chem.* 2020, 8, 595616. [CrossRef] [PubMed]

17. Naseri, M.; Fotouhi, L.; Ehsani, A. Recent Progress in the Development of Conducting Polymer-Based Nanocomposites for Electrochemical Biosensors Applications: A Mini-Review. *Chem. Sci. Rec.* 2018, 18, 599–618. [CrossRef] [PubMed]

18. El-Said, W.A.; Abdelshakour, A.; Choi, J.-H.; Choi, J.-W. Application of Conducting Polymer Nanostructures to Electrochemical Biosensors. *Molecules* 2020, 25, 307. [CrossRef] [PubMed]

19. Das, T.K.; Prusty, S. Review on Conducting Polymers and Their Applications. *Polym. Plast. Technol. Eng.* 2012, 51, 1487–1500. [CrossRef]

20. Stenger-Smith, J.D. Intrinsically electrically conducting polymers. Synthesis, characterization, and their applications. *Prog. Polym. Sci.* 1998, 23, 57–79. [CrossRef]

21. Epstein, A.J. Electrically Conducting Polymers: Science and Technology. *MRS Bull.* 2004, 29, 70. [CrossRef]

22. Svirskis, D.; Travas-Sejdic, J.; Rodgers, A.; Garg, S. Electrochemically controlled drug delivery based on intrinsically conducting polymers. *J. Control. Release* 2010, 146, 6–15. [CrossRef]

23. Otero, T.F.; Martinez, V.; Arias-Pardilla, J. Biomimetic electrochemistry from conducting polymers. A review Artificial muscles, electrically conducting polymers. *Biomacromolecules* 2008, 9, 2541–2554. [CrossRef] [PubMed]

24. Wong, J.Y.; Langer, R.; Ingverg, D.E. Electrically conducting polymers can noninvasively control the shape and growth of mammalian cells. *Proc. Natl. Acad. Sci. USA* 1994, 91, 3201–3204. [CrossRef] [PubMed]

25. Adelouj, S.B.; Wallace, G.G. Conducting Polymers and the Bioanalytical Sciences: New Tools for Biomolecular Communications-A Review. *Analyst* 1996, 121, 699–703. [CrossRef]

26. Park, Y.; Jung, J.; Chang, M. Research Progress on Conducting Polymer-Based Biomedical Applications. *Appl. Sci.* 2019, 9, 1070. [CrossRef]

27. Hackett, A.J.; Malmström, J.; Travas-Sejdic, J. Functionalization of conducting polymers for biointerface applications. *Prog. Polym. Sci.* 2017, 70, 18–33. [CrossRef]

28. Bhattacharyaa, A.; Misra, B.N. Grafting: A versatile means to modify polymers. Techniques, factors and applications. *Prog. Polym. Sci.* 2004, 29, 767–814. [CrossRef]

29. Czerwiec, T.; Renevier, N.; Michel, H. Low-temperature plasma-assisted nitriding. *Surf. Coat. Technol.* 2000, 131, 267–277. [CrossRef]

30. Foest, R.; Schmidt, M.; Becker, K. Microplasmas, an emerging field of low-temperature plasma science and technology. *Int. J. Mass Spectrom.* 2006, 248, 87–102. [CrossRef]

31. Fu, W.; Zhang, C.; Nie, C.; Li, X.; Yan, Y. A high efficiency low-temperature microwave-driven atmospheric pressure plasma jet. *Appl. Phys. Lett.* 2019, 114, 254106. [CrossRef]

32. Zeghidiou, H.; Assadi, A.A.; Khellaf, N.; Djelal, H.; Amrane, A.; Ritmi, S. Photocatalytic Performance of CuxO/TiO2 Deposited by HiPIMS on Polyester under Visible Light LEDs:Oxidants, Ions Effect, and Reactive Oxygen Species Investigation. *Materials* 2019, 12, 412. [CrossRef]

33. Tran, H.D.; D’Arcy, J.M.; Wang, Y.; Beltramo, P.J.; Strong, V.A.; Kaner, R.B. The oxidation of aniline to produce “polyaniline”: A process yielding many different nanoscale structures. *J. Mater. Chem.* 2011, 21, 3534–3550. [CrossRef]
36. Lapkowski, M.; Berrada, K.; Quillard, S.; Louarn, G.; Lefrant, S.; Pron, A. Electrochemical Oxidation of Polyaniline in Nonaqueous Electrolytes: “In Situ” Raman Spectroscopic Studies. *Macromolecules* **1995**, *28*, 1233–1238. [CrossRef]

37. Zeghioud, H.; Lamouri, S.; Safidine, Z.; Belbachir, M. Chemical synthesis and characterization of highly soluble conducting polyaniline in mixtures of common solvents. *J. Serb. Chem. Soc.* **2015**, *80*, 917–931. [CrossRef]

38. Jiang, Z.; Jiang, Z.; Yu, X.; Meng, Y. Preparation of Proton Exchange Membranes by a Plasma Polymerization Method and Application in Direct Methanol Fuel Cells (DMFCs). *Plasma Processes Polym.* **2010**, *7*, 382–389. [CrossRef]

39. Choukourov, A.; Biederman, H.; Slavinska, D.; Hanley, L.; Grinevich, A.; Boldyryeva, H.; Mackova, A. Mechanistic Studies of Plasma Polymerization of Allylamine. *J. Phys. Chem. B* **2005**, *109*, 23086–23095. [CrossRef] [PubMed]

40. Cech, V.; Studynka, J.; Janos, F.; Perina, V. Influence of Oxygen on the Chemical Structure of Plasma Polymer Films Deposited from a Mixture of Tetravinylsilane and Oxygen Gas. *Plasma Processes Polym.* **2007**, *4*, S776–S780. [CrossRef]