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Two-in-One Sensor Based on PV4D4-Coated TiO_2 Films for Food Spoilage Detection and as a Breath Marker for Several Diseases

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Abstract: Certain molecules act as biomarkers in exhaled breath or outgassing vapors of biological systems. Specifically, ammonia (NH_3) can serve as a tracer for food spoilage as well as a breath marker for several diseases. H_2 gas in the exhaled breath can be associated with gastric disorders. This initiates an increasing demand for small and reliable devices with high sensitivity capable of detecting such molecules. Metal-oxide gas sensors present an excellent tradeoff, e.g., compared to expensive and large gas chromatographs for this purpose. However, selective identification of NH_3 at the parts-per-million (ppm) level as well as detection of multiple gases in gas mixtures with one sensor remain a challenge. In this work, a new two-in-one sensor for NH_3 and H_2 detection is presented, which provides stable, precise, and very selective properties for the tracking of these vapors at low concentrations. The fabricated 15 nm TiO_2 gas sensors, which were annealed at 610 °C, formed two crystal phases, namely anatase and rutile, and afterwards were covered with a thin 25 nm PV4D4 polymer nanolayer via initiated chemical vapor deposition (iCVD) and showed precise NH_3 response at room temperature and exclusive H_2 detection at elevated operating temperatures. This enables new possibilities in application fields such as biomedical diagnosis, biosensors, and the development of non-invasive technology.

Keywords: sensors; ammonia; hydrogen; PV4D4 polymer

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1. Introduction

Modern technologies are advancing every day, and with them the medical field and it's diagnostic part, as well as the fields of health and food safety. To improve diagnosis, it is helpful to link the patients health states with data obtained from different health analyzing technologies. To improve diagnosis, it is helpful to link the patients' health states with data obtained from different health analyzing technologies. In this regards, an interesting example of such an advance can be seen in a previous study [1] where a system of computer-aided diagnostics improved the results of a plain X-ray using machine learning. Another good example is an interpretable deep learning system in the study of Kai Jin et al. [2], where the main goal was to classify the epiretinal membrane for different optical coherence tomography devices, which, however, still needs further research, as its potential demonstrated. As a matter of fact, even previous and further studies, which will be seen in this work, have as their main goal minimal to non-invasive diagnosis, where much of the potential lies with gas detectors and sensors.

The introduction of novel gas detectors with rapid and efficient gas concentration detection capabilities has been a major focus for different application fields [3]. One of the current techniques that is being intensively developed is the breath test [4], which uses different methods, technologies, and analytical systems. These include different sampling injections methods and devices such as gas chromatographs (GC) but also sensor-based devices. While the GC might be a convenient method for breath analysis, it cannot detect H_2 and is a rather expensive technique [5] compared to the field of fast-developing metal-oxide-based sensors. Metal-oxide sensors appear in many different forms, such as coated/uncoated with polymers [6], titanium carbide sensors [3], and many other compounds, e.g., titanium. Human breath contains many biomarkers, and it can show an entire series of different diseases and disorders [7–10].

However, there are not enough technologies and solid-state devices for the detection of these tracers, even though a recent approach to the gas detecting methods is surface plasmon resonance through optical means, where, for instance, a thin film of SnO_2 and polypyrrole (PPy) were prepared for sensing ammonia [11]. In the same working field, another method for ammonia detection is shown in the study [12] through a colorimetric analysis is used to visualize manipulations of the localized resonance of the surface Plasmon band of silver nanoparticles. In this study, it was also shown that a smartphone can be used as a rapid, inexpensive method for real-time detection of ammonia by monitorin color intensity variations of an RGB analysis. In another study [13], a metal–organic framework was used as a colorimetric sensor for ammonia detection. On the other hand, metal-oxide-based sensors have yet to show their true potential and high efficiency through fast gas detection, as they are coated with polymers for adapting to different measurement conditions, therefore tuning up their properties. Many articles [5,7–10,14–16] offer a good base for further development of H_2 gas and NH_3 vapor in human breath detectors based on different sensors mostly because these two have shown a specific approach to diagnosis. For instance, H_2 gas is usually associated with gastric disorders such as lactose intolerance and bacterial overgrowth within the small bowel and for diagnosing rapid passage of food through the small bowel [5], while in food industry H_2 is usually mentioned as a spoilage factor to canned food [17]. NH_3 vapor can usually be associated with kidney failure, which can be characterized at its early stages by detection of its concentration in exhaled breath. Another example of the use of NH_3 detection is its recognition as a biomarker in the field of hepatic kidney diseases [18]. On the other hand, NH_3 gas also serves as a spoiling marker for food rich in proteins [19]. Thus, further development of H_2- and NH_3-detecting sensors is required, as they provide a growing potential for enhanced detection and analysis in the biomedical diagnosis field.

While many authors are developing new methods for NH_3, H_2, and other vapor/gas detection [3,5,18], in this study, a sensor based on a TiO_2 nanolayer fully covered with a Poly(1,3,5,7-tetramethyl-tetravinylcyclotetrasiloxane) (PV4D4) thin film is proposed as a two-in-one sensor with high potential for NH_3 and H_2 gas detection. The PV4D4 thin film on top of the sensor was fabricated by initiated chemical vapor deposition (iCVD) in the same way as in our previous study [6]. Attributed to its solvent-free nature and CVD-typical growth characteristics, the iCVD process enables a precise coverage of good-quality, tailored polymer nanolayers on the lower nanoscale on specimens with a large surface area or on more complex geometries [20,21] such as the TiO_2 structures in this study. TiO_2 has been proven in several articles as a compatible H_2 detector. It shows a series of responses to different gases such as 2-propanol, n-butanol, ethanol, and acetone [22]. Consequently, the challenge is to maintain a high selectivity for H_2. In another study, thin nano-sprayed layers of TiO_2 show a variation in responses depending on the film thickness [23], having a high selectivity for H_2 at 15 nm but without a clear response to NH_3. At 20 nm thickness, it shows a better response to NH_3 but is still lacking high selectivity towards H_2. In this context, some authors have reported on the functionalization of the sensor with different noble metals such as Au [23], while others have coated sensors with a conductive polymer layer [24]. Our previous study [6] showed impressive results of the influence of iCVD-deposited PV4D4 thin films and their influence on the sensor performance. It can improve the selectivity for different gases regarding different structures.

The motivation to use a PV4D4-coated TiO_2 gas sensor in this study is to demonstrate a potential two-in-one sensor and its protection from ambient and efficiency. The developed two-in-one sensors exhibit high selectivity for certain gases at relatively low operating temperatures and high selectivity for other gases at higher operating temperatures. Since the applied polymer layer on top of the TiO_2 films shows an effect on the selectivity of H_2 and NH_3, depending on the working temperature, it can be applied as a potential two-in-one sensor for breath analysis. Although further studies on different biomarkers related to different diseases and disorders are needed, the proposed sensor can provide new pathways in the field of medical diagnosis and the development of non-invasive technology.

References

1. Sato, Y.; Takegami, Y.; Asamoto, T.; Ono, Y.; Hidetoshi, T.; Goto, R.; Kitamura, A.; Honda, S. Artificial Intelligence Improves the Accuracy of Residents in the Diagnosis of Hip Fractures: A Multicenter Study. *BMC Musculoskelet. Disord.* **2021**, *22*, 407. [CrossRef]
2. Jin, K.; Yan, Y.; Wang, S.; Yang, C.; Chen, M.; Liu, X.; Terasaki, H.; Yeo, T.-H.; Singh, N.G.; Wang, Y.; et al. IERM: An Interpretable Deep Learning System to Classify Epiretinal Membrane for Different Optical Coherence Tomography Devices: A Multi-Center Analysis. *J. Clin. Med.* **2023**, *12*, 400. [CrossRef]
3. Khakbaz, P.; Moshayedi, M.; Hajian, S.; Soleimani, M.; Narakathu, B.B.; Bazuin, B.J.; Pourfath, M.; Atashbar, M.Z. Titanium Carbide MXene as NH_3 Sensor: Realistic First-Principles Study. *J. Phys. Chem. C* **2019**, *123*, 29794–29803. [CrossRef]
4. Samotaev, N.; Etrekova, M.; Litvinov, A.; Mikhailov, A. Selective Ammonia Detection by Field Effect Gas Sensor as an Instrumentation Basis for HP-Infection Primary Diagnosis. In Proceedings of the 5th International Conference on Nanotechnologies and Biomedical Engineering, Online, 3–5 November 2021; Tiginyanu, I., Sontea, V., Railean, S., Eds.; Springer International Publishing: Cham, Switzerland, 2022; pp. 177–184, ISBN 978-3-030-92328-0.
5. Shin, W. Medical Applications of Breath Hydrogen Measurements. *Anal. Bioanal. Chem.* **2014**, *406*, 3931–3939. [CrossRef]
6. Schröder, S.; Ababii, N.; Brînză, M.; Magariu, N.; Zimoch, L.; Bodduluri, M.T.; Strunskus, T.; Adelung, R.; Faupel, F.; Lupan, O. Tuning the Selectivity of Metal Oxide Gas Sensors with Vapor Phase Deposited Ultrathin Polymer Thin Films. *Polymers* **2023**, *15*, 524. [CrossRef] [PubMed]
7. Cloarec, D.; Bornet, F.; Gouilloud, S.; Barry, J.L.; Salim, B.; Galmiche, J.P. Breath Hydrogen Response to Lactulose in Healthy Subjects: Relationship to Methane Producing Status. *Gut* **1990**, *31*, 300–304. [CrossRef] [PubMed]
8. Urita, Y.; Watanabe, T.; Ishihara, S.; Maeda, T.; Sasaki, Y.; Hike, K.; Miura, Y.; Nanami, T.; Arai, K.-I.; Koshino, H.; et al. Breath Hydrogen and Methane Levels in a Patient with Volvulus of the Sigmoid Colon. *J. Breath Res.* **2008**, *2*, 037025. [CrossRef]
9. Liu, F.; Kondo, T.; Toda, F. Measurement of Breath Hydrogen. *Nagoya J. Health Phys. Fit. Sport.* **1992**, *15*, 33–37.
10. Kim, K.-H.; Jahan, S.A.; Kabir, E. A Review of Breath Analysis for Diagnosis of Human Health. *TrAC Trends Anal. Chem.* **2012**, *33*, 1–8. [CrossRef]
11. Gahlot, A.P.S.; Paliwal, A.; Kapoor, A. Exploitation of SnO_2/Polypyrrole Interface for Detection of Ammonia Vapors Using Conductometric and Optical Techniques: A Theoretical and Experimental Analysis. *Sensors* **2022**, *22*, 7252. [CrossRef]
12. Amirjani, A.; Fatmehsari, D.H. Colorimetric Detection of Ammonia Using Smartphones Based on Localized Surface Plasmon Resonance of Silver Nanoparticles. *Talanta* **2018**, *176*, 242–246. [CrossRef] [PubMed]

13. Sotirov, S.; Demirci, S.; Marudova, M.; Sahiner, N. Trimesic Acid-Based Co(II) MOFs as Colorimetric Sensor for Detection of Ammonia Gas. *IEEE Sens. J.* **2022**, *22*, 3903–3910. [CrossRef]
14. Simren, M. Use and Abuse of Hydrogen Breath Tests. *Gut* **2006**, *55*, 297–303. [CrossRef] [PubMed]
15. Shin, J.; Choi, S.-J.; Lee, I.; Youn, D.-Y.; Park, C.O.; Lee, J.-H.; Tuller, H.L.; Kim, I.-D. Thin-Wall Assembled SnO_2 Fibers Functionalized by Catalytic Pt Nanoparticles and Their Superior Exhaled-Breath-Sensing Properties for the Diagnosis of Diabetes. *Adv. Funct. Mater.* **2013**, *23*, 2357–2367. [CrossRef]
16. Di Stefano, M.; Corazza, G.R. Role of Hydrogen and Methane Breath Testing in Gastrointestinal Diseases. *Dig. Liver Dis. Suppl.* **2009**, *3*, 40–43. [CrossRef]
17. Maity, A.; Raychaudhuri, A.K.; Ghosh, B. High Sensitivity NH_3 Gas Sensor with Electrical Readout Made on Paper with Perovskite Halide as Sensor Material. *Sci. Rep.* **2019**, *9*, 7777. [CrossRef]
18. Gleason, K.K. Nanoscale Control by Chemically Vapour-Deposited Polymers. *Nat. Rev. Phys.* **2020**, *2*, 347–364. [CrossRef]
19. Coclite, A.M.; Howden, R.M.; Borrelli, D.C.; Petruczok, C.D.; Yang, R.; Yagüe, J.L.; Ugur, A.; Chen, N.; Lee, S.; Jo, W.J.; et al. 25th Anniversary Article: CVD Polymers: A New Paradigm for Surface Modifi Cation and Device Fabrication. *Adv. Mater.* **2013**, *25*, 5392–5423. [CrossRef]
20. Lupan, O.; Postica, V.; Ababii, N.; Reimer, T.; Shree, S.; Hoppe, M.; Polonskyi, O.; Sontea, V.; Chemnitz, S.; Faupel, F.; et al. Ultra-Thin TiO_2 Films by Atomic Layer Deposition and Surface Functionalization with Au Nanodots for Sensing Applications. *Mater. Sci. Semicond. Process* **2018**, *87*, 44–53. [CrossRef]
21. Ababii, N.; Hoppe, M.; Shree, S.; Vahl, A.; Ulfa, M.; Pauporté, T.; Viana, B.; Cretu, V.; Magariu, N.; Postica, V.; et al. Effect of Noble Metal Functionalization and Film Thickness on Sensing Properties of Sprayed TiO_2 Ultra-Thin Films. *Sens. Actuators A Phys.* **2019**, *293*, 242–258. [CrossRef]
22. Lee, W.-C.; Kim, K.-B.; Gurudatt, N.G.; Hussain, K.K.; Choi, C.S.; Park, D.-S.; Shim, Y.-B. Comparison of Enzymatic and Non-Enzymatic Glucose Sensors Based on Hierarchical Au-Ni Alloy with Conductive Polymer. *Biosens. Bioelectron.* **2019**, *130*, 48–54. [CrossRef] [PubMed]
23. Wang, P.; Shao, Z.; Ulfa, M.; Pauporté, T. Insights into the Hole Blocking Layer Effect on the Perovskite Solar Cell Performance and Impedance Response. *J. Phys. Chem. C* **2017**, *121*, 9131–9141. [CrossRef]
24. Schröder, S.; Strunskus, T.; Rehders, S.; Gleason, K.K.; Faupel, F. Tunable Polytetrafluoroethylene Electret Films with Extraordinary Charge Stability Synthesized by Initiated Chemical Vapor Deposition for Organic Electronics Applications. *Sci. Rep.* **2019**, *9*, 2237. [CrossRef] [PubMed]
25. Valiev, M.; Bylaska, E.J.; Govind, N.; Kowalski, K.; Straatsma, T.P.; Van Dam, H.J.J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T.L.; et al. NWChem: A Comprehensive and Scalable Open-Source Solution for Large Scale Molecular Simulations. *Comput. Phys. Commun.* **2010**, *181*, 1477–1489. [CrossRef]
26. Siebert, L.; Wolff, N.; Ababii, N.; Terasa, M.-I.; Lupan, O.; Vahl, A.; Duppel, V.; Qiu, H.; Tienken, M.; Mirabelli, M.; et al. Facile Fabrication of Semiconducting Oxide Nanostructures by Direct Ink Writing of Readily Available Metal Microparticles and Their Application as Low Power Acetone Gas Sensors. *Nano Energy* **2020**, *70*, 104420. [CrossRef]
27. Lupan, O.; Cretu, V.; Postica, V.; Ababii, N.; Polonskyi, O.; Kaidas, V.; Schütt, F.; Mishra, Y.K.; Monaico, E.; Tiginyanu, I.; et al. Enhanced Ethanol Vapour Sensing Performances of Copper Oxide Nanocrystals with Mixed Phases. *Sens. Actuators B Chem.* **2016**, *224*, 434–448. [CrossRef]
28. Lau, K.K.S.; Gleason, K.K. Initiated Chemical Vapor Deposition (ICVD) of Poly(Alkyl Acrylates): An Experimental Study. *Macromolecules* **2006**, *39*, 3688–3694. [CrossRef]
29. Schröder, S.; Hinz, A.M.; Strunskus, T.; Faupel, F. Molecular Insight into Real-Time Reaction Kinetics of Free Radical Polymerization from the Vapor Phase by In-Situ Mass Spectrometry. *J. Phys. Chem. A* **2021**, *125*, 1661–1667. [CrossRef]
30. Socrates, G. Alkane Group Residues: C-H Group. In *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*; John Wiley & Sons Ltd.: Chichester, UK, 2004; pp. 50–67. ISBN 978-0-470-09307-8.
31. Socrates, G. Organic Silicon Compounds. In *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*; John Wiley & Sons Ltd.: Chichester, UK, 2004; pp. 241–246. ISBN 978-0-470-09307-8.
32. Ohsaka, T.; Izumi, F.; Fujiki, Y. Raman Spectrum of Anatase, TiO_2. *J. Raman Spectrosc.* **1978**, *7*, 321–324. [CrossRef]
33. Enachi, M.; Lupan, O.; Braniste, T.; Sarua, A.; Chow, L.; Mishra, Y.K.; Gedamu, D.; Adelung, R.; Tiginyanu, I. Integration of Individual TiO_2 Nanotube on the Chip: Nanodevice for Hydrogen Sensing. *Phys. Status Solidi—Rapid Res. Lett.* **2015**, *9*, 171–174. [CrossRef]
34. Wetchakun, N.; Incessungvorn, B.; Wetchakun, K.; Phanichphant, S. Influence of Calcination Temperature on Anatase to Rutile Phase Transformation in TiO_2 Nanoparticles Synthesized by the Modified Sol–Gel Method. *Mater. Lett.* **2012**, *82*, 195–198. [CrossRef]
35. Kameya, Y.; Yabe, H. Optical and Superhydrophilic Characteristics of TiO_2 Coating with Subwavelength Surface Structure Consisting of Spherical Nanoparticle Aggregates. *Coatings* **2019**, *9*, 547. [CrossRef]
36. Morsella, M.; D'Alessandro, N.; Lanterna, A.E.; Scaiano, J.C. Improving the Sunscreen Properties of TiO_2 through an Understanding of Its Catalytic Properties. *ACS Omega* **2016**, *1*, 464–469. [CrossRef] [PubMed]
37. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D.W. Understanding TiO_2 Photocatalysis: Mechanisms and Materials. *Chem. Rev.* **2014**, *114*, 9919–9986. [CrossRef] [PubMed]

38. Fogue, C.; Lemdani, M.; Huart, C. Nasal Chemosensory Tests: Biomarker between Dementia with Lewy Bodies and Parkinson Disease Dementia. *Rhinol. J.* **2020**, *58*, 605–609. [CrossRef] [PubMed]
39. Lupan, O.; Postica, V.; Wolff, N.; Polonskyi, O.; Duppel, V.; Kaidas, V.; Lazari, E.; Ababii, N.; Faupel, F.; Kienle, L.; et al. Localized Synthesis of Iron Oxide Nanowires and Fabrication of High Performance Nanosensors Based on a Single Fe_2O_3 Nanowire. *Small* **2017**, *13*, 1602868. [CrossRef] [PubMed]
40. Nair, S.; Cope, K.; Terence, R.H.; Diehl, A.M. Obesity and Female Gender Increase Breath Ethanol Concentration: Potential Implications for The Pathogenesis of Nonalcoholic Steatohepatitis. *Am. J. Gastroenterol.* **2001**, *96*, 1200–1204. [CrossRef]
41. Koureas, M.; Kirgou, P.; Amoutzias, G.; Hadjichristodoulou, C.; Gourgoulianis, K.; Tsakalof, A. Target Analysis of Volatile Organic Compounds in Exhaled Breath for Lung Cancer Discrimination from Other Pulmonary Diseases and Healthy Persons. *Metabolites* **2020**, *10*, 317. [CrossRef]
42. Hwang, L.; Low, K.; Khoshini, R.; Melmed, G.; Sahakian, A.; Makhani, M.; Pokkunuri, V.; Pimentel, M. Evaluating Breath Methane as a Diagnostic Test for Constipation-Predominant IBS. *Dig. Dis. Sci.* **2010**, *55*, 398–403. [CrossRef]
43. Afzal, A.; Cioffi, N.; Sabbatini, L.; Torsi, L. NO_x Sensors Based on Semiconducting Metal Oxide Nanostructures: Progress and Perspectives. *Sens. Actuators B Chem.* **2012**, *171–172*, 25–42. [CrossRef]
44. Lepselter, M.P.; Sze, S.M. Silicon Schottky Barrier Diode with Near-Ideal I-V Characteristics. *Bell Syst. Tech. J.* **1968**, *47*, 195–208. [CrossRef]
45. NIST Standard Reference Database Number 69. Available online: https://webbook.nist.gov/chemistry/ (accessed on 19 February 2023).
46. Lupan, O.; Santos-Carballal, D.; Ababii, N.; Magariu, N.; Hansen, S.; Vahl, A.; Zimoch, L.; Hoppe, M.; Pauporté, T.; Galstyan, V.; et al. $TiO_2/Cu_2O/CuO$ Multi-Nanolayers as Sensors for H_2 and Volatile Organic Compounds: An Experimental and Theoretical Investigation. *ACS Appl. Mater. Interfaces* **2021**, *13*, 32363–32380. [CrossRef]
47. Chang, S. Oxygen Chemisorption on Tin Oxide: Correlation between Electrical Conductivity and EPR Measurements. *J. Vac. Sci. Technol.* **1980**, *17*, 366–369. [CrossRef]
48. Lenaerts, S.; Roggen, J.; Maes, G. FT-IR Characterization of Tin Dioxide Gas Sensor Materials under Working Conditions. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **1995**, *51*, 883–894. [CrossRef]
49. Cheng, C.; Zhang, H.; Li, F.; Yu, S.; Chen, Y. High Performance Ammonia Gas Detection Based on $TiO_2/WO_3{\cdot}H_2O$ Heterojunction Sensor. *Mater. Chem. Phys.* **2021**, *273*, 125098. [CrossRef]
50. Gao, J.; Qin, J.; Chang, J.; Liu, H.; Wu, Z.-S.; Feng, L. NH_3 Sensor Based on 2D Wormlike Polypyrrole/Graphene Heterostructures for a Self-Powered Integrated System. *ACS Appl. Mater. Interfaces* **2020**, *12*, 38674–38681. [CrossRef]
51. Kim, S.J.; Koh, H.-J.; Ren, C.E.; Kwon, O.; Maleski, K.; Cho, S.-Y.; Anasori, B.; Kim, C.-K.; Choi, Y.-K.; Kim, J.; et al. Metallic $Ti_3C_2T_x$ MXene Gas Sensors with Ultrahigh Signal-to-Noise Ratio. *ACS Nano* **2018**, *12*, 986–993. [CrossRef]
52. Srirattanapibul, S.; Nakarungsee, P.; Issro, C.; Tang, I.-M.; Thongmee, S. Enhanced Room Temperature NH_3 Sensing of RGO/Co_3O_4 Nanocomposites. *Mater. Chem. Phys.* **2021**, *272*, 125033. [CrossRef]
53. Beniwal, A. Sunny Electrospun SnO_2/PPy Nanocomposite for Ultra-Low Ammonia Concentration Detection at Room Temperature. *Sens. Actuators B Chem.* **2019**, *296*, 126660. [CrossRef]
54. Malook, K.; Khan, H.; Shah, M.; Haque, I.-U.-. Highly Selective and Sensitive Response of Polypyrrole–MnO_2 Based Composites towards Ammonia Gas. *Polym. Compos.* **2019**, *40*, 1676–1683. [CrossRef]
55. Ho, T.A.; Jun, T.-S.; Kim, Y.S. Material and NH_3-Sensing Properties of Polypyrrole-Coated Tungsten Oxide Nanofibers. *Sensors Actuators B Chem.* **2013**, *185*, 523–529. [CrossRef]
56. Thi Hien, H.; Thi Anh Thu, D.; Quang Ngan, P.; Hong Thai, G.; Thanh Trung, D.; Trung, T.; Minh Tan, M.; Truong Giang, H. High NH_3 Sensing Performance of NiO/PPy Hybrid Nanostructures. *Sens. Actuators B Chem.* **2021**, *340*, 129986. [CrossRef]
57. Tan, Y.; Du, B.; Liang, C.; Guo, X.; Zheng, H.; Liu, P.; Yang, X.; Li, S.; Jin, B.; Sun, J. Improving Anti-Humidity Property of a SnO_2-Based Chemiresistive Hydrogen Sensor by a Breathable and Hydrophobic Fluoropolymer Coating. *Langmuir* **2022**, *38*, 13833–13840. [CrossRef] [PubMed]
58. Piiper, J. Respiratory Gas Exchange at Lungs, Gills and Tissues: Mechanisms and Adjustments. *J. Exp. Biol.* **1982**, *100*, 5–22. [CrossRef]
59. Yan, L.; Yin-He, S.; Qian, Y.; Zhi-Yu, S.; Chun-Zi, W.; Zi-Yun, L. Method of Reaching Consensus on Probability of Food Safety Based on the Integration of Finite Credible Data on Block Chain. *IEEE Access* **2021**, *9*, 123764–123776. [CrossRef]
60. Yousefi, H.; Su, H.-M.; Imani, S.M.; Alkhaldi, K.; Filipe, C.D.M.; Didar, T.F. Intelligent Food Packaging: A Review of Smart Sensing Technologies for Monitoring Food Quality. *ACS Sens.* **2019**, *4*, 808–821. [CrossRef]
61. Yuan, Z.; Bariya, M.; Fahad, H.M.; Wu, J.; Han, R.; Gupta, N.; Javey, A. Trace-Level, Multi-Gas Detection for Food Quality Assessment Based on Decorated Silicon Transistor Arrays. *Adv. Mater.* **2020**, *32*, 1908385. [CrossRef]
62. Evancho, G.M.; Tortorelli, S.; Scott, V.N. Microbiological Spoilage of Canned Foods. In *Compendium of the Microbiological Spoilage of Foods and Beverages*; Sperber, W.H., Doyle, M.P., Eds.; Springer: New York, NY, USA, 2009; pp. 185–221, ISBN 978-1-4419-0826-1.

63. Wang, Y.; Liu, S.; Yang, X.; Zhang, J.; Zhang, Y.; Liu, X.; Zhang, H.; Wang, H. Effect of Germination on Nutritional Properties and Quality Attributes of Glutinous Rice Flour and Dumplings. *J. Food Compos. Anal.* **2022**, *108*, 104440. [CrossRef]
64. Zhang, Y.; Zhang, S.; Yang, X.; Wang, W.; Liu, X.; Wang, H.; Zhang, H. Enhancing the Fermentation Performance of Frozen Dough by Ultrasonication: Effect of Starch Hierarchical Structures. *J. Cereal Sci.* **2022**, *106*, 103500. [CrossRef]