

Article

Gas Sensitivity Improvements of Nanowire Hexadecafluorinated Iron Phthalocyanines by Thermal Vacuum Annealing

Carmen L. Metzler ¹, Soraya Y. Flores ², John Cruz Lozada ¹, Jean González ¹, Sebastián Suárez Schmidt ¹, Danilo Barrionuevo ³, Peter Feng ², Wilfredo Otaño ³, Luis Fonseca ^{2,*} and Dalice M. Piñero Cruz ^{1,*}

¹ Department of Chemistry, University of Puerto Rico, Río Piedras, San Juan, PR 00931, USA; carmen.metzler@upr.edu (C.L.M.); john.cruz1@upr.edu (J.C.L.); jean.gonzalez@upr.edu (J.G.); ssuarezschmidt@unr.edu (S.S.S.)

² Department of Physics, University of Puerto Rico, Río Piedras, San Juan, PR 00925, USA; soraya.flores@upr.edu (S.Y.F.); peter.feng@upr.edu (P.F.)

³ Department of Physics, University of Puerto Rico, Cayey, PR 00736, USA; danilo.barrionuevo@upr.edu (D.B.); wilfredo.otano@upr.edu (W.O.)

* Correspondence: luis.fonseca@upr.edu (L.F.); dalice.pinero@upr.edu (D.M.P.C.)

Abstract: In the quest for more sensitive gas sensors, researchers have studied how heating the sensors, using UV light, and thermally annealing sensors improve performance. During thermal annealing, the heating process can improve the crystallinity of the material while also increasing the electrode and sensing material interactions to create more available active sites and thus improve sensor performance. Hexadecafluorinated iron (II) phthalocyanine (FePcF₁₆) nanowires have high sensitivity towards NH₃ selectively, and thermally annealing the NWs after the deposition can further improve the sensing response and recovery. For this reason, the effect of annealing FePcF₁₆ NWs at different temperatures was studied to optimize these systems. In this work, FePcF₁₆ NWs were synthesized using physical vapor deposition (PVD) to deposit on interdigitated electrodes. The NWs were characterized by SEM, EDS, PXRD, FTIR, and Raman spectroscopy to confirm their purity. The sensors were annealed at different temperatures, inserted into a gas sensing chamber, and exposed to 1 ppm NH₃ in air, and the electrical current was measured. The results show that the optimized FePcF₁₆ NWs have excellent sensing properties, with a 58% increase in response towards NH₃ after a stepwise annealing at 300 °C confirming these systems are good prospective candidates for sensing NH₃ at room temperature.

Keywords: metal phthalocyanines; gas sensors; thermal annealing; nanowires; ammonia



Received: 13 December 2024

Revised: 14 February 2025

Accepted: 25 February 2025

Published: 7 March 2025

Citation: Metzler, C.L.; Flores, S.Y.; Cruz Lozada, J.; González, J.; Suárez Schmidt, S.; Barrionuevo, D.; Feng, P.; Otaño, W.; Fonseca, L.; Piñero Cruz, D.M. Gas Sensitivity Improvements of Nanowire Hexadecafluorinated Iron Phthalocyanines by Thermal Vacuum Annealing. *Chemosensors* **2025**, *13*, 95. <https://doi.org/10.3390/chemosensors13030095>

Copyright: © 2025 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

Atmospheric contaminants like toxic gases and fine particles can have dangerous effects on living beings, jeopardizing the quality of life of the exposed population [1]. By implementing systems for the detection and monitoring of trace amounts of dangerous gases such as ammonia (NH₃) or nitrogen dioxide (NO₂), the health consequences that arise through prolonged exposure can be reduced. While the average concentration of NH₃ in the atmosphere is in the range of 0.1 to 5 ppb, areas with increased agriculture or industry can have significantly higher NH₃ concentrations of 100 ppb or higher [2]. According to the Occupational Safety and Health Administration (OSHA), the exposure limit of NH₃ is 25 ppm for 8 h or 35 ppm for 10 min [3]. However, even low-concentration long-term inhalation can result in 20 to 30% dissolution in the mucus and lead to obstructive airway disease [4]. Since NH₃ can be detrimental to the health of the population even at

low exposure limits, it is imperative to develop sensitive gas sensors to warn populations before they are exposed to dangerous gases for extended periods of time. While there are a number of metal oxide gas sensors, they are limited by high operating temperatures (approximately 300 °C), and operating these sensors at room temperature limits their sensitivity [5,6]. Moreover, while polymer-based sensors have fast response times, they often are less sensitive, with lower limits of detection around 10 to 50 ppm [7]. Therefore, reliable gas sensors with higher sensitivity are needed to monitor the concentration of these pollutants.

Metal phthalocyanines (MPcs) are synthetic analogues of porphyrin developed in the 1920s as a dye [8]. Since then, researchers have discovered how useful these materials are as solar cells, electrocatalysts, and gas sensors due to their inherent tunability. Additionally, MPcs have had impressive results in electronics, chemical sensing, and energy conversion and storage [9]. Substituted metal phthalocyanines (MPcX_{4,8,16}) are generally planar complexes in which transition metals such as Mn, Fe, Co, Ni, Cu, and Zn are coordinated in a tetradentate manner to the inner four nitrogens of the Pc ligand [10–12]. While unsubstituted MPcs are generally p-type semiconductors, this behavior can easily be changed based on the substituents added to the peripheral aryl rings and/or the coordinating metal to convert the MPc from a p-type to an n-type semiconductor [13]. For example, the addition of fluorine to the aryl rings converts the MPc to an n-type semiconductor, while unsubstituted bis-phthalocyanato lanthanide complexes have ambipolar behavior [14,15]. Another benefit of MPcs is their highly conjugated π systems from the aromaticity within the molecule. These conjugated aromatic systems allow for changes in the electronic resistance within the materials when the metal center coordinates gaseous NH₃ or NO₂, thus triggering a measurable electrochemical response. Hexadecafluorinated iron phthalocyanine (FePcF₁₆) is an n-type semiconductor whose outer fluorine substituents allow for a favorable electron transfer [14]. The more electronegative fluorine substituents pull electrons from the aromatic rings towards themselves, changing the distribution of electron density. The electron withdrawing towards the outer edges of the complex leaves the metal center wanting for electrons [16]. Not only does this permit a rich array of chemical interactions but it also allows the FePcF₁₆ to have increased gas sensitivity and selectivity towards reducing gases like NH₃ [14].

To improve the previously reported high sensitivity of these complexes, the materials can be annealed after synthesis [17]. Annealing is a common process in materials science and specifically in the formation of metal alloys. In this area, researchers have found significant changes in the structural and physical properties of the materials, leading to improvement for the materials' intended purposes [18]. In the case of gas-sensitive materials, significant improvement has been seen in the sensitivity of metal oxides towards H₂ after annealing [19,20]. For example, annealing SnO₂ increases the sensitivity of the material and improves the response and recovery times simultaneously [19]. This is thought to be due to the increase in the SnO₂ crystal size, which allows for an easier electron pathway through the material. Similarly, annealing Ga-doped ZnO thin films at 700 °C increased the sensitivity, response time, and recovery time towards both acetone and ethanol [21]. X-Ray Diffraction (XRD) spectroscopy was used to study these changes in the crystalline lattice and gain insight as to how physical changes correlate to changes in the chemiresistive response. In both cases, the annealing showed more narrow and intense diffractions for the annealed samples when compared to the pristine samples, suggesting that the sample increases in crystallinity after annealing [19,21]. Researchers have also studied the effect of annealing on MPc systems like PbPc, GaPcCl, and TiPcCl₂ and found improvements in the materials' structural, optical, and gas sensing properties with an increase in conductivity after annealing the thin films [22–24]. In MPcs used for gas sensing, the changes caused

by annealing give rise to electrical and structural improvements, leading to increased sensitivity and reducing response time. These improvements occur both in thin films of oxide materials and in Pcs, making thermal annealing of FePcF₁₆ NWs an attractive option for improving its gas sensing capabilities.

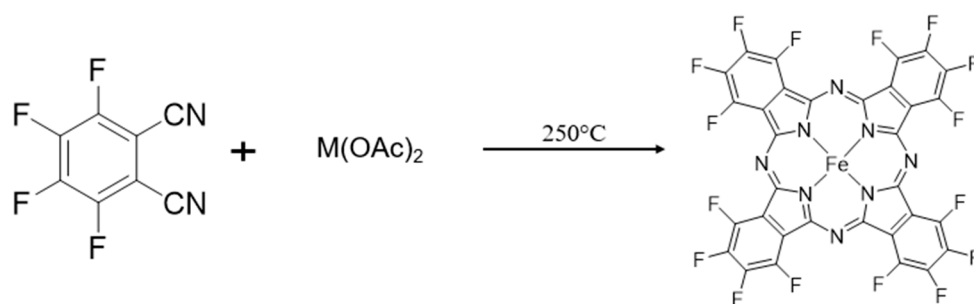
This research focused on the improvement of previously reported FePcF₁₆ nanowires for NH₃ sensing by observing any changes to the gas sensing behavior after the materials underwent thermal annealing. The results obtained from this work revealed that fluorinated metal phthalocyanines are not only reliable sensors with high selectivity and sensitivity but that adding a thermal annealing step prior to the gas sensing stage can enhance the response and recovery of our sensors, improving the functionality of these materials as gas sensors.

2. Materials and Methods

FePcF₁₆ is synthesized using a simple template reaction performed under inert conditions, resulting in a crystalline product. The fluorinated samples can then be deposited directly onto gold interdigitated electrodes using physical vapor deposition. This generates a sensor made of a portable substrate with nanostructures that branch across and connect the terminal of the electrodes. Then, the sensor can be tested in a gas sensing apparatus and measurements of the electric response can be carried out as the gas comes into contact with the material surface. Adding an additional annealing step can improve the performance of these materials even more.

2.1. Synthesis of FePcF₁₆ Powder

FePcF₁₆ was synthesized by first grinding fluorinated phthalonitrile and the metal acetate salt in a 1:1 stoichiometric ratio, then heating the solids to 250 °C as shown in Scheme 1 [14]. Excess metal (II) acetate and tetrafluorophthalonitrile were washed from the solid with water and hexane, respectively, via vacuum filtration. Final impurities were removed by Soxhlet extraction with distilled acetone, where the impurities were insoluble and thus left in a solid state. The tetrafluorophthalonitrile and iron (II) acetate were bought from TCI chemicals with a 98.0% purity and Alfa Aesar with a 95% purity, respectively.



Scheme 1. Synthesis and structure of MPcF₁₆.

2.2. Synthesis of MPcF₁₆ Nanowires

The synthesis of the FePcF₁₆ NWs was performed in a two-phase oven (MTI Corporation, Richmond, CA, USA, model OFT-1200X-II) with a quartz tube of 0.05 m in diameter and 1.2 m in length. The quartz tube is connected to a Trivec D168B mechanical pump. To synthesize the nanowires, the substrates (Al, quartz, and silicon) were mounted in the physical vapor deposition (PVD) chamber approximately 13 cm away from ~20 mg of the precursor material. The chamber was set to a constant pressure of 5 torr (monitored using an Inficon PSG55x pressure gauge; Balzers, LIE) and a constant N₂ gas flux of 100 sccm using an MKS 946 Multigas controller (Andover, MA, USA). The temperature of the oven

was increased to 120 °C for 20 min to eliminate any humidity that might have entered the tube furnace. After 20 min, the temperature was increased again to 420 °C using a 6.67 °C/min rate. This temperature was maintained for the duration of the 1 h deposition time. During this time, the FePcF₁₆ sublimed, traveled with the N₂ flux down the tube furnace, and deposited on the substrates as the gas cooled (~130 °C). Finally, the substrates containing FePcF₁₆ nanowires were vacuum annealed at 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C using a heating rate of 4.67 °C/min and a pressure of 10^{−2} torr for various lengths of time to study the effect of annealing on the gas sensing capabilities. The FePcF₁₆ NWs were characterized using SEM/EDS, PXRD, Raman spectroscopy, and UV/Vis spectroscopy (shown in Figure S1) to show the purity of the NWs and investigate whether the FePcF₁₆ underwent a phase change.

3. Results and Discussion

3.1. SEM Images of FePcF₁₆ Nanowires

The synthesized FePcF₁₆ nanowires deposited on aluminum substrates were characterized via SEM to verify the identity and structure of the compounds at the nanometric scale (Figure 1). These experiments were performed using a JEOL JSM-7500F HR field emission SEM with a JOEL JEM-9310 focused ion beam system. The images showed slightly different arrays of nanowires, and the EDS analyses demonstrated consistent intensity peaks for Fe and F at all the temperatures (shown in Figure S2). Additionally, the SEM images show the reorientation of the nanowires with the increase in the temperature. This reorientation is often accompanied by an increase in crystallinity of the material [25,26]. The realignment of the nanowires could result in the increase in available active sites for gas coordination or a shifting of the nanowire connections on the electrode itself.

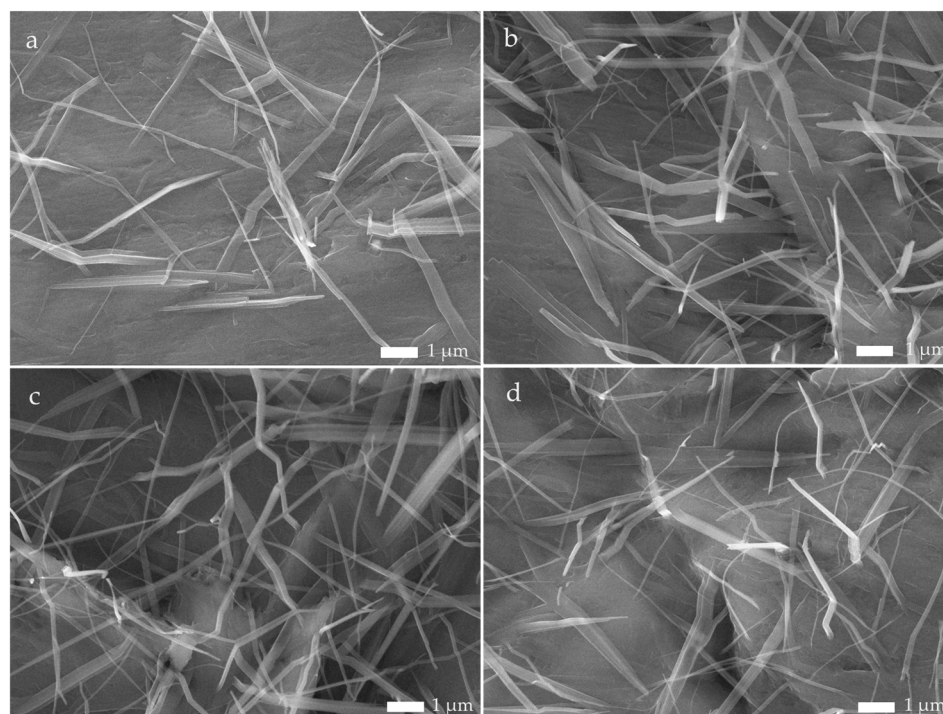


Figure 1. SEM images of FePcF₁₆ NWs without annealing (a) and after annealing for 30 min at 100 °C (b), 200 °C (c), and 300 °C (d).

3.2. Analysis of XRD Patterns

The XRD experiments were performed on a Rigaku SmartLabs instrument irradiating the FePcF₁₆ NWs deposited on a quartz substrate at 40 kV and 40 nA. The XRD diffrac-

tograms confirmed the identity of the complexes after the PVD and annealing processes with distinct peaks along the 2θ axis. The most intense peak for FePcF₁₆ occurred within the $2\theta = 6.25 - 6.50^\circ$, with other noticeable peaks along the value ranges of $(12.60-12.67^\circ)$, $(21.30-21.60^\circ)$, $(31.93-31.98^\circ)$, and $(44.47-44.73^\circ)$, taken at each of the temperatures, as shown in Figure 2. The diffraction at 6° and 12° are characteristic of the 100 and 002 planes of the β phase FePcF₁₆ [14]. In the case of the conversion of the FePcF₁₆ from powder to nanowires, there is a clear phase change that occurs as the FePcF₁₆ goes from the α phase to the β phase [14]. However, it can be clearly seen in Figure 2a that no additional phase change occurs during the thermal annealing process, even at temperatures above 200°C . Additionally, there is some loss in the intensity of the annealed diffraction peaks as compared to the pristine NWs. While this is commonly attributed to decreasing crystallinity, there is a slight narrowing in the diffractions showing the increase in the crystallinity of the NWs, as shown in Figure 2b. Further study showed that annealing at temperatures above 300°C caused the FePcF₁₆ material to sublime and leave the substrate. Therefore, when taken in combination with the peak narrowing, the decreasing intensity of the diffraction peaks is attributed to a small amount of sublimation of the FePcF₁₆ material rather than decreasing crystallinity of the NWs. Additionally, the crystallite size was calculated for each annealing temperature using the Scherrer equation, taking the shape constant, K , to be 0.89 (shown in Table S1) [27–30]. These results show that, as opposed to what is seen in the literature, the crystallite size does not increase significantly with the annealing [22,25]. Therefore, the increase in crystallinity seen is attributed to the elimination of voids, impurities, and surface-level oxygen [24].

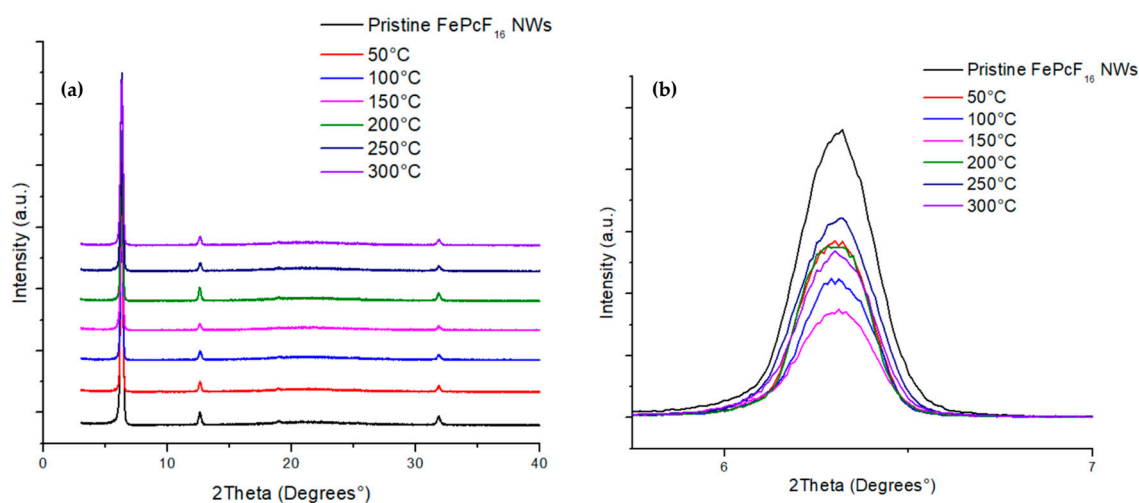


Figure 2. (a) XRD diffractograms of the FePcF₁₆ NW at the various annealed temperatures showing no change in phase. (b) Zoom of the FePcF₁₆ NW 6° diffraction showing the slight peak narrowing attributed with an increase in crystallinity.

3.3. Raman of FePcF₁₆ NW

The lack of physical and chemical changes in the material was confirmed by spectroscopic characterization of the FePcF₁₆ NWs deposited on quartz substrate via Raman spectroscopy. The experiments were performed using a T64000 Raman spectrometer from Jobin Yvon-Horiba with a triple monochromator in subtractive mode and equipped with a CCD detector. An Olympus microscope with 80x objective in backscattering mode was used to focus the Coherent Argon Innova 70C laser beam using a wavelength of 514.53 nm and a power of 5 mW on the sample. First and foremost, no structural change occurred in the NW materials during the thermal annealing process. The data of the FePcF₁₆ NWs shown in Figure 3 consists of the pristine NWs and the NWs annealed at 100°C , 200°C ,

and 300 °C. These data are representative of the results seen at 50 °C, 150 °C, and 250 °C (all spectra shown in Figure S3). In these spectra, the same distinctive MPc stretches from 1400 to 1600 cm^{-1} associated with the C=N and C=C region can be seen, as well as the macro-ring or imidazole ring peaks seen from 600 cm^{-1} to 1250 cm^{-1} . Much as in the case of the XRD experiments, a decrease in the intensity can be seen as the samples were annealed. Once again, this is attributed to a small amount of the materials subliming and leaving the system rather than damage to the system.

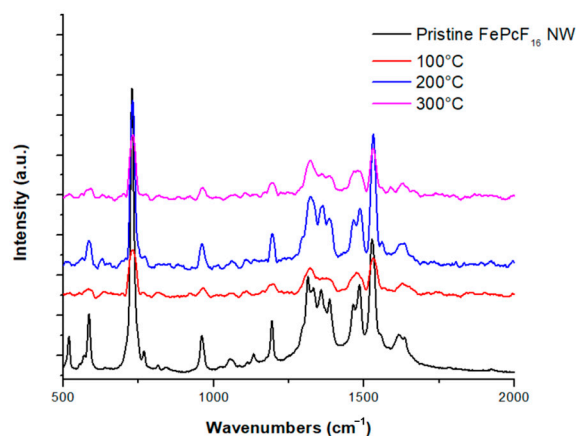


Figure 3. Raman spectra of the annealed FePcF₁₆ NWs showing that no physical or structural changes occurred in the NWs during the thermal annealing process. These spectra are representative of all the thermal annealing temperatures, which can be seen in Figure S3.

3.4. Effect of Annealing on the FePcF₁₆ NWs

The gas sensing experiments were performed by placing the FePcF₁₆ NWs, deposited and annealed on gold interdigitated electrodes (IDEs), into a specifically designed and pre-tested chamber. The IDEs used were commercially available Micrux Thin-Film gold interdigitated electrode (5/5 μm electrode/gap) with a glass substrate and a SU8/PI resin insulating layer. The gas test system consists of a gas detection chamber (MMR Technologies LTMP-4), where the sensing devices were at room temperature (75 °F/24 °C/297 K) and connected with tungsten probes inside the chamber. A Keithley 6487 picoammeter/voltage source was used to evaluate the sensor response and was controlled by LabVIEW 8.5 software. This device supplies 5 V and measures the electric current's intensity as a time function during exposure to airflow with and without contaminant gas. The desired contaminant gas concentration is established by combining an air flow (compressed air) and a test gas flow (100 ppm ammonia/nitrogen) in the appropriate ratio to define the final concentration in parts per billion by volume. An MKS GE50A mass flow controller is used in this process, which the MKS 946 vacuum system controller monitors. The total flow was 500 sccm. The FePcF₁₆ NW systems equilibrated in air with a flow rate of 500 sccm for 2 h, and then were exposed to 1 ppm NH₃ diluted in air with a flow rate of 500 sccm for 1 h at room temperature. The response of the NW systems to the analyte gases was measured by continuous recording of the flow. After the NH₃ gas flow was turned off, the FePcF₁₆ system recovered for 2 h in air with the same flow rate previously mentioned. The response of the FePcF₁₆ NW system was calculated as a percentage using $(I_{60} - I_0)/I_0 \times 100$, and the recovery was calculated using $(I_{60} - I_{100})/(I_{60} - I_0) \times 100$, where I_0 is taken to be the current when the gas is turned on, I_{60} is taken to be the current when the gas is turned off, and finally I_{100} is the current after 40 min equilibrating in air post NH₃ exposure.

Prior to the annealing, the IDEs with FePcF₁₆ NWs were subjected to sensitivity measurements which served as a ground base comparison to observe the changes that occurred in their sensitivity. To understand whether time or temperature play a larger role

in improving the gas sensing capabilities of the FePcF₁₆ NWs, two types of measurements were performed on the various systems synthesized. The first type of measurement used a singular IDE for all the annealing temperatures (these experiments are denoted “same sample” in the graphical legends), and the gas sensing response was measured after each annealing step. The second set of experiments consisted of using different IDEs for each annealing temperature and measuring the response before and after annealing (these experiments are denoted “different samples” in the graphical legends). For all these experiments, the NWs were annealed from 50 °C to 300 °C in 50° increments and their gas sensing capabilities measured at 1 ppm of NH₃ in air. The results of the experiments showed that different annealing temperatures had direct effects on the sensing capabilities of the sensor, and there was an increase in sensitivity of the FePcF₁₆ systems after annealing when exposed to 1 ppm of NH₃. To study whether temperature or annealing time has more influence on the sensor response, FePcF₁₆ NWs were annealed for different lengths of time as well as at different temperatures. The results of these experiments show that the length of the annealing time and the annealing temperature both play a significant role in the improvement of the sensor response.

Preliminary experiments consisted of FePcF₁₆ NW samples, deposited on an IDE, annealed for 2 h with 50 °C increments as mentioned above. For these experiments, the NWs’ gas sensing response was measured, the NWs were annealed, and the response was remeasured with all of the annealing occurring to the sample NWs on one IDE. A 2 h anneal time was used for these experiments after consulting the literature and finding reports for the improvement of gas sensors with 2 h annealing [31,32]. The results of these first experiments (shown in Figure 4a) show a slight improvement in the response towards NH₃ with some of the annealing temperatures. For instance, when annealing at 50 °C and 300 °C, there is an improvement in the response from 16% to 17% and 26%, respectively. Additionally, annealing the sample at 300 °C shows a clear increase in the response of the sample, while annealing at 200 °C consistently shows the lowest response towards NH₃. These results are interesting considering that 250 °C has commonly been used as the thermal annealing temperature for MPc thin films to improve various properties due to the phase change at 200 °C [23,33,34]. In the case of the as-prepared FePcF₁₆ NWs, XRD diffractograms show no phase change occurring. Since annealing the NWs allows them to reorient their position and can change the NW–NW and sublayer–electrode contacts, as proposed in other related systems, experimental results suggest that such annealing-promoted effects optimize at 300 °C for the FePcF₁₆ NW-based sensors [35]. Additionally, thermal annealing is known to eliminate oxygen impurities, voids, and other flaws within the crystalline materials; therefore, thermally annealing the materials could cause an increase in the purity of the FePcF₁₆ NWs, opening more active sites to receive the gaseous NH₃ and thus increasing the sensor performance [24].

To further study the effect of the length of time annealed on the systems, FePcF₁₆ NWs were annealed at 150 °C for 12 h and compared to the 2 h annealing experiments. As can be seen in Figure 4b, annealing the samples for 12 h made little difference in the response as compared to the samples with only 2 h of thermal annealing, as the response remained at ~13% in both cases. This shows that while the time the NWs are annealed does influence the gas sensing capabilities, there is a saturation time after which there is not enough of an improvement in the response and recovery to justify the length of time annealed. After determining the upper time threshold for improving the sensor performance, the annealing time was shortened to determine the lower time threshold. For these experiments, two samples were annealed for 30 min and 1 hour, respectively, at the previously described temperatures. The gas sensing performance was measured before and after each annealing step. These experiments resulted in a decrease in the current post annealing; however,

there was an increase in the response and recovery of the samples, as seen in Figure 5. The relative response of each annealing temperature was then compared to the relative response of the pristine FePcF₁₆ NWs for was length of annealing time, as shown in Table 1. In fact, annealing for one hour decreased the relative response, while annealing the samples for 30 min resulted in an increase in the relative response. Additionally, annealing at 300 °C consistently showed an increase in the response as opposed to the other annealing temperatures, which often decreased the response towards NH₃. This shows that the shorter annealing times are more optimal for the FePcF₁₆ NW-based sensors.

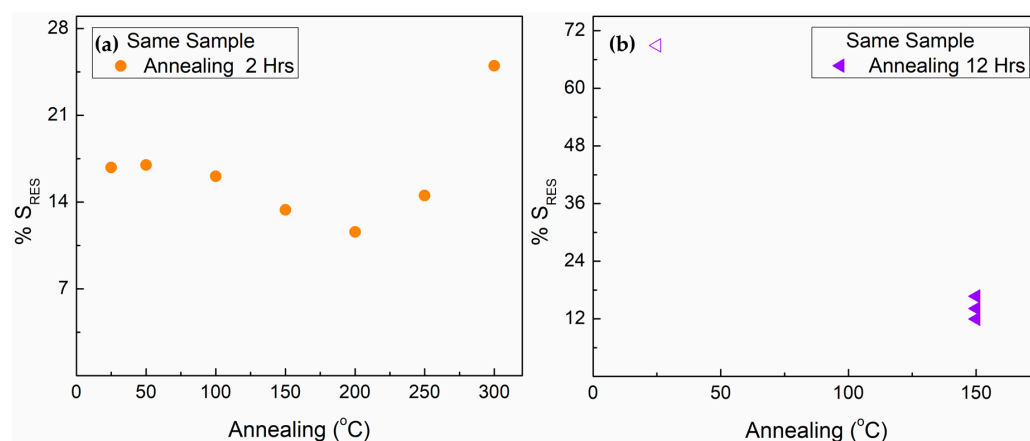


Figure 4. (a) Response of the FePcF₁₆ NW systems at each annealing temperature when annealing for 2 h each. (b) Response of the FePcF₁₆ NWs annealed at 150 °C for 12 h, showing no difference between annealing for 12 h and 2 h. The response at 25 °C is the response of the non-annealed systems; these are represented by the hollow shapes for additional clarity.

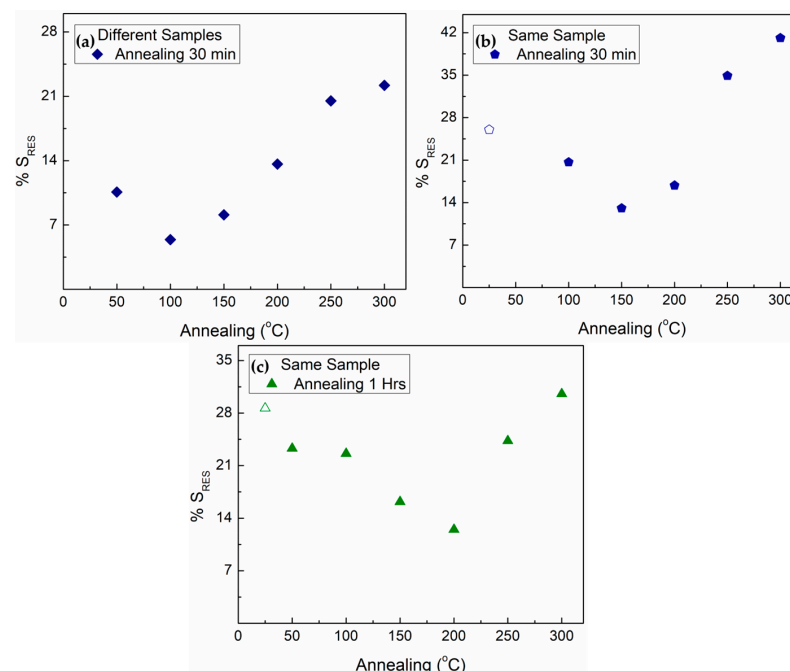
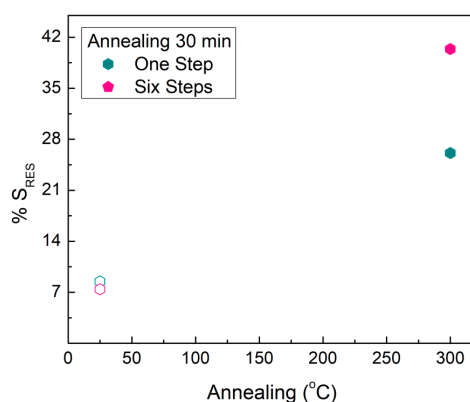


Figure 5. (a) Percent response of the FePcF₁₆ NWs at each annealing temperature when annealing for 30 min on one IDE. (b) Percent response of the FePcF₁₆ NWs at each annealing temperature when annealing for 30 min on different IDEs. (c) Percent response of the FePcF₁₆ NWs at each annealing temperature when annealing for 1 h, where the response at 25 °C is the response of the non-annealed systems indicated with hollow shapes for clarity.

Table 1. Percent change in the response of the annealed FePcF₁₆ NWs deposited on IDEs when exposed to NH₃.

Annealing Temperature	30 Min Annealing	1 h Annealing	2 h Annealing	12 h Annealing
50 °C	−15.5%	−18.2%	3.4%	-
100 °C	−21.11%	−20.6%	−3.6%	-
150 °C	−50.2%	−43.7%	−19.4%	−76.9%
200 °C	−36.18%	−56.5%	−30.5%	-
250 °C	32.1%	−15.9%	−12.8%	-
300 °C	57.7%	6.5%	51.3%	-

Upon further consideration of the experimental design, it was noted that the experiments performed in the 30 min and 1 h trials were using compounding annealing steps. That is to say, there was one sample annealed at each of the temperatures, resulting in six annealing steps in total. Since this could very well cause the differences in the sensor performance seen in Figure 5a,b, two more IDEs were prepared with FePcF₁₆ NWs and annealed at 300 °C for 30 min and in a stepwise manner with a slow ramp. The stepwise annealing used the same heating ramp as described before, but the heating was performed by stopping at 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, and finally 300 °C for 30 min each during the same annealing experiment, resulting in a 5 h stepwise thermal annealing. The results of these experiments are shown in Figure 6 and Figure S4, where the difference between the stepwise ramp and the 30 min annealing time can clearly be seen. In fact, the compounding annealing resulted in a 30% increase in the response compared to that of the 30 min annealing. One reason for this increase could be that the stepwise annealing of the materials slows the annealing process and allows the NWs to reorient into the optimal lattice. Additionally, it has been shown that the thermal annealing process can decrease the activation energy of the adsorption/desorption processes, allowing for faster response and recovery times [22]. The graphs in Figure S5 corroborate these findings, showing an increase in conductivity after annealing the samples to 300 °C. It is possible the slower annealing ramp could help with the removal of excess water or defects in the crystalline lattice, resulting in more available active sites in which gas coordination can occur. The removal of these defects in combination with the increase in crystallinity decrease in adsorption activation energy due to the thermal annealing process could combine to allow for the improvement seen in the FePcF₁₆ NW systems.

**Figure 6.** Comparison of the response of the FePcF₁₆ NWs annealed for 30 min at 300 °C and the NWs that underwent stepwise annealing from 50 °C to 300 °C, stopping at 50° intervals for 30 min. The response at 25 °C is the response of the non-annealed systems indicated with a hollow shape for clarity.

After comparing the response of all the annealed FePcF₁₆ NW systems with the non-annealed NWs, the recovery of the systems was compared. Figure 7 shows the difference between the recoveries of all of the annealed and non-annealed systems. The recovery of the annealed FePcF₁₆ NW systems was consistently increased. Similar to the response, annealing at 200 °C shows the least improvement in the recovery, no matter the amount of time annealed. Additionally, annealing FePcF₁₆ NWs for 30 min or 1 h has the most improvement on the recovery of the systems, going from 27% to 50% and 32% to 70% recovery, respectively. The optimized sensors underwent long-term stability and humidity sensitivity testing (Figures S10 and S11, respectively), and it was determined that while there is an expected decrease in response over time, the sensitivity in the presence of humidity only slightly decreases. This shows that not only does annealing FePcF₁₆ NWs improve the sensing response towards NH₃ but it also improves the recovery of the systems, allowing them to be reusable gas sensing materials.

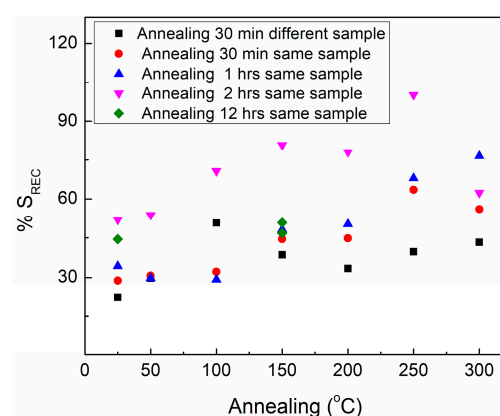


Figure 7. Comparison of the percent recovery for each of the synthesized FePcF₁₆ NW systems at annealing temperatures from 50 °C to 300 °C at 50 °C intervals, where the 25 °C points are the non-annealed NWs.

4. Conclusions

Overall, this work shows the benefits of annealing MPcF₁₆ nanowire-based sensors to improve their gas sensing capabilities. The compounding annealing from 50 °C to 300 °C increased the percent response and recovery towards NH₃ the most, with a 30% increase in the response and a 20% increase in the recovery when compared to the non-compounding annealing. This is thought to be due to the removal of oxygen impurities and defects from the crystalline system in addition to the increase in available active sites from possible changes in the orientation of the nanowires and surface modifications after thermal annealing. Additionally, annealing FePcF₁₆ nanowires for more than 1 h without a stepwise annealing process results in little improvement of the gas sensing capabilities of the sensor. Therefore, the optimal annealing for these materials is using a heating ramp of 4.6 °C/minute and stopping for 30 min at each temperature, with the ending temperature being 300 °C. Finally, this optimized sensor was tested for stability over time and sensitivity with increased humidity and the sensors retained sensitivity towards NH₃. Overall, the compounding annealing process decreases the rate at which the wires are annealed giving them more time to convert into the optimal orientation while also increasing the crystallinity of the wires. Thus, these combined effects result in the performance improvement of the FePcF₁₆ NWs when exposed to NH₃.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemosensors13030095/s1>, Figure S1: Solid state UV/Vis spectra of the FePcF₁₆ pre and post thermal annealing; Figure S2: SEM image of the FePcF₁₆ NWs without annealing with the SEM magnification included; Figure S3: Plot of the percentage of each element within the FePcF₁₆ NWs obtained by elemental analysis showing the purity of the NWs before and after thermal annealing; Figure S4: Spectra of the FePcF₁₆ NWs annealed for 2 hours at various temperatures showing the lack of physical, structural, or phase change in the nanowires after annealing; Figure S5: Normalized response of the FePcF₁₆ NWs before and after they were annealed; Figure S6: Current response of the FePcF₁₆ NWs before and after they were annealed at temperatures ranging from 50 °C to 300 °C in 50 °C increments on different samples; Figure S7: Normalized response of the FePcF₁₆ NWs before and after they were annealed at temperatures ranging from 50 °C to 300 °C in 50 °C increments on the same sample; Figure S8: Normalized response of the FePcF₁₆ NWs before and after they were annealed to 300 °C for 30 minutes and to 300 °C in six steps; Figure S9: Response of the FePcF₁₆ NWs towards CH₄, CO, H₂, and NO₂ showing the selectivity of the NWs; Figure S10: Normalized gas sensing of the FePcF₁₆ NWs when first measured in September compared to the repetition of the same experiment four months later in January; Figure S11: FePcF₁₆ NW sensor response conducting the experiment at 70% relative humidity versus 80% relative humidity; Table S1: Size of the FePcF₁₆ NW crystallites as calculated by the Sherrer Equation; Table S2: Table of the interdigitated electrodes with annealed FePcF₁₆ NWs.

Author Contributions: C.L.M. performed the deposition, annealing, and characterization of the NWs, as well as the gas-sensing experiments, and was the major contributor to the manuscript writing. S.Y.F. contributed to the deposition, annealing, and characterization of the NWs, gas-sensing experiments, and analyzed the gas sensing data. J.C.L. contributed to the preparation and synthesis of starting materials for MPc. J.G. contributed to the methodology, preparation and synthesis of starting materials for MPc. S.S.S. contributed to the deposition and annealing of the NWs. D.B. and W.O. contributed their knowledge of XRD analysis and crystallographic data collection. P.F. contributed to the gas-sensing resources. L.F. and D.M.P.C. designed and directed the research, supervised the work herein, revised the data, and contributed to the manuscript writing and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the RISE Grant Program (grant number: 5R25GM061151-22) and NSF-CREST CIRE2N (grant number: HRD-1736093). XRD experiments were performed on a Rigaku Smartlabs funded by the NSF (MRI award number: 2215247) and the Single Crystal X-ray Diffraction Facility (NSF grant number CHE-1626103).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are contained within the article and the Supplementary Materials.

Acknowledgments: The authors acknowledge the Materials and Characterization Center (MCC) (located in the Molecular Science Research Center).

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

References

1. How Air Pollution is Destroying Our Health. Available online: <https://www.who.int/news-room/spotlight/how-air-pollution-is-destroying-our-health> (accessed on 20 May 2022).
2. Pogány, A.; Balslev-Harder, D.; Braban, C.F.; Cassidy, N.; Ebert, V.; Ferracci, V.; Hieta, T.; Leuenberger, D.; Martin, N.A.; Pascale, C.; et al. A Metrological Approach to Improve Accuracy and Reliability of Ammonia Measurements in Ambient Air. *Meas. Sci. Technol.* **2016**, *27*, 110512. [CrossRef]
3. Permissible Exposure Limits—Annotated Tables. Available online: <https://www.osha.gov/annotated-pels/table-z-1> (accessed on 23 September 2023).
4. Padappayil, R.P.; Borger, J. Ammonia Toxicity. Available online: <https://www.ncbi.nlm.nih.gov/books/NBK546677/> (accessed on 23 January 2024).

5. Jung, H.T. The Present and Future of Gas Sensors. *ACS Sens.* **2022**, *7*, 912–913. [[CrossRef](#)] [[PubMed](#)]
6. Dey, A. Semiconductor Metal Oxide Gas Sensors: A Review. *Mater. Sci. Eng. B* **2018**, *229*, 206–217. [[CrossRef](#)]
7. Kwak, D.; Lei, Y.; Maric, R. Ammonia Gas Sensors: A Comprehensive Review. *Talanta* **2019**, *204*, 713–730. [[CrossRef](#)] [[PubMed](#)]
8. Wright, J.D. Gas Adsorption on Phthalocyanines and Its Effects on Electrical Properties. *Prog. Surf. Sci.* **1989**, *31*, 1–60. [[CrossRef](#)]
9. Meng, Z.; Aykanat, A.; Mirica, K.A. Welding Metallophthalocyanines into Bimetallic Molecular Meshes for Ultrasensitive, Low-Power Chemiresistive Detection of Gases. *J. Am. Chem. Soc.* **2019**, *141*, 2046–2053. [[CrossRef](#)]
10. Myers, J.F.; Rayner Canham, G.W.; Lever, B.P. Higher Oxidation Level Phthalocyanine Complexes of Chromium, Iron, Cobalt, and Zinc. Phthalocyanine Radical Species. *Inorg. Chem.* **1975**, *14*, 461–468. [[CrossRef](#)]
11. Achar, B.N.; Jayasree, P.K. Novel “synthetic Metals” Based on Symmetrically Tetrasubstituted Nickel Phthalocyanines. *Synth. Met.* **1999**, *104*, 101–106. [[CrossRef](#)]
12. Debnath, A.K.; Samanta, S.; Singh, A.; Aswal, D.K.; Gupta, S.K.; Yakhmi, J.V. Parts-per-Billion Level Chlorine Sensors with Fast Kinetics Using Ultrathin Cobalt Phthalocyanine Films. *Chem. Phys. Lett.* **2009**, *480*, 185–188. [[CrossRef](#)]
13. Parkhomenko, R.G.; Sukhikh, A.S.; Klyamer, D.D.; Krasnov, P.O.; Gromilov, S.; Kadem, B.; Hassan, A.K.; Basova, T.V. Thin Films of Unsubstituted and Fluorinated Palladium Phthalocyanines: Structure and Sensor Response toward Ammonia and Hydrogen. *J. Phys. Chem. C* **2017**, *121*, 1200–1209. [[CrossRef](#)]
14. Flores, S.Y.; Gonzalez-Espiet, J.; Cintrón, J.; Villanueva, N.D.J.; Camino, F.E.; Kisslinger, K.; Cruz, D.M.P.; Rivera, R.D.; Fonseca, L.F. Fluorinated Iron and Cobalt Phthalocyanine Nanowire Chemiresistors for Environmental Gas Monitoring at Parts-per-Billion Levels. *ACS Appl. Nano Mater.* **2022**, *5*, 4688–4699. [[CrossRef](#)]
15. Kong, X.; Dong, Z.; Wu, Y.; Li, X.; Chen, Y.; Jiang, J. High Sensitive Ambipolar Response towards Oxidizing NO₂ and Reducing NH₃ Based on Bis(Phthalocyaninato) Europium Semiconductors. *Chin. J. Chem.* **2016**, *34*, 975–982. [[CrossRef](#)]
16. Jiang, H.; Ye, J.; Hu, P.; Wei, F.; Du, K.; Wang, N.; Ba, T.; Feng, S.; Kloc, C. Fluorination of Metal Phthalocyanines: Single-Crystal Growth, Efficient N-Channel Organic Field-Effect Transistors, and Structure-Property Relationships. *Sci. Rep.* **2014**, *4*, 7573. [[CrossRef](#)]
17. Alonzo-Medina, G.M.; González-González, A.; Sacedón, J.L.; Oliva, A.I. Understanding the Thermal Annealing Process on Metallic Thin Films. *IOP Conf. Ser. Mater. Sci. Eng.* **2013**, *45*, 012013. [[CrossRef](#)]
18. Shen, J.; Chen, B.; Wan, J.; Shen, J.; Li, J. Materials Science & Engineering A Effect of Annealing on Microstructure and Mechanical Properties of an Al-Mg-Sc-Zr Alloy. *Mater. Sci. Eng. A* **2022**, *838*, 142821. [[CrossRef](#)]
19. Yang, Y.; Maeng, B.; Jung, D.G.; Lee, J.; Kim, Y.; Kwon, J.B.; An, H.K.; Jung, D. Annealing Effects on SnO₂ Thin Film for H₂ Gas Sensing. *Nanomaterials* **2022**, *12*, 3227. [[CrossRef](#)]
20. Zhang, H.; He, F.; Che, Y.; Song, Y.; Zhou, M.; Ding, D. Effect of Annealing Treatment on Response Characteristics of Pd-Ni Alloy Based Hydrogen Sensor. *Surf. Interfaces* **2023**, *36*, 102597. [[CrossRef](#)]
21. Ramola, R.C.; Negi, S.; Rawat, M.; Singh, R.C.; Singh, F. Annealing Effects on Gas Sensing Response of Ga-Doped ZnO Thin Films. *ACS Omega* **2021**, *6*, 11660–11668. [[CrossRef](#)]
22. Liu, C.J.; Hsieh, J.C.; Ju, Y.H. Response Characteristics of Lead Phthalocyanine Gas Sensor: Effect of Operating Temperature and Postdeposition Annealing. *J. Vac. Sci. Technol. A Vac. Surf. Film.* **1996**, *14*, 753–756. [[CrossRef](#)]
23. Elesh, E.; Mohammed, Z. Morphological, Linear and Nonlinear Properties of Gallium Phthalocyanine Chloride Annealed Thin Films. *Optik* **2020**, *219*, 165176. [[CrossRef](#)]
24. Abdelhamid, S.M.; Dongol, M.; Elhady, A.F.; Abuelwafa, A.A. Role of Vacuum Annealing on the Structural, Optical Properties and DC Conductivity of Titanium (IV) Phthalocyanine Dichloride Thin Films. *Phys. Scr.* **2023**, *98*, 125960. [[CrossRef](#)]
25. Kheiri, F.; Soleimani, V.; Ghasemi, M.; Mokhtari, A. The Microstructure, Optical and Gas Sensing Properties of Bilayer TiO₂/ZnO Systems in Terms of Annealing Temperature. *Mater. Sci. Semicond. Process.* **2021**, *121*, 105462. [[CrossRef](#)]
26. Chen, L.Y.; Hunter, G.W.; Neudeck, P.G.; Knight, D. Surface and Interface Properties of PdCr/SiC Schottky Diode Gas Sensor Annealed at 425°C. *Solid. State. Electron.* **1998**, *42*, 2209–2214. [[CrossRef](#)]
27. Stegmann, C.; Muench, F.; Rauber, M.; Hottes, M.; Brötz, J.; Kunz, U.; Lauterbach, S.; Kleebe, H.J.; Ensinger, W. Platinum Nanowires with Pronounced Texture, Controlled Crystallite Size and Excellent Growth Homogeneity Fabricated by Optimized Pulsed Electrodeposition. *RSC Adv.* **2014**, *4*, 4804–4810. [[CrossRef](#)]
28. Kumar, N.; Kumar, R.; Kumar, S.; Chakarvarti, S.K. Structural and Electrical Studies of Template Synthesized Copper Nanowires. *Curr. Appl. Phys.* **2014**, *14*, 1547–1552. [[CrossRef](#)]
29. Štengl, V.; Bakardjieva, S.; Murafa, N.; Večerníková, E.; Šubrt, J.; Balek, V. Preparation and Characterization of Titania Based Nanowires. *J. Nanoparticle Res.* **2007**, *9*, 455–470. [[CrossRef](#)]
30. Kurtulus, O.; Li, Z.; Mews, A.; Pietsch, U. X-Ray Investigation of CdSe Nanowires. *Phys. Status Solidi Appl. Mater. Sci.* **2009**, *206*, 1752–1756. [[CrossRef](#)]
31. Datir, A.; Koinkar, P.; Chakane, S. Effects of Heat Annealing on the Gas Sensing Properties of Spin Coated Unsubstituted Copper Phthalocyanine Films. *Adv. Mater. Res.* **2015**, *1110*, 241–245. [[CrossRef](#)]

32. Klyamer, D.; Sukhikh, A.; Bonegardt, D.; Krasnov, P.O.; Popovetskiy, P.; Basova, T. Thin Films of Chlorinated Vanadyl Phthalocyanines as Active Layers of Chemiresistive Sensors for the Detection of Ammonia. *Micromachines* **2023**, *14*, 1773. [[CrossRef](#)]
33. Jafari, M.J.; Azim-Araghi, M.E.; Barhemat, S.; Riyazi, S. Effect of Post-Deposition Annealing on Surface Morphology and Gas Sensing Properties of Palladium Phthalocyanine Thin Films. *Surf. Interface Anal.* **2012**, *44*, 601–608. [[CrossRef](#)]
34. Popielarski, P.; Mosińska, L.; Skowronski, L.; Szczesny, R.; Figà, V.; Naparty, M.; Derkowska-Zielinska, B. Influence of Heat Treatment on Surface, Structural and Optical Properties of Nickel and Copper Phthalocyanines Thin Films. *Int. J. Mol. Sci.* **2022**, *23*, 11055. [[CrossRef](#)] [[PubMed](#)]
35. King, B.; Moorthy, S.G.; Lesniewska, E.; Meunier-Prest, R.; Bouvet, M.; Lessard, B.H. Modulating the Majority Charge Carrier Type and Performance of Organic Heterojunction Ammonia Sensors by Increasing Peripheral Fluorination of the Silicon Phthalocyanine Sublayer. *Sens. Actuators B Chem.* **2024**, *408*, 135507. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.