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Integrated Capacitive- and Resistive-Type Bimodal Relative Humidity Sensor Based on 5,10,15,20-Tetraphenylporphyrinatonicel(II) (TPPNI) and Zinc Oxide (ZnO) Nanocomposite

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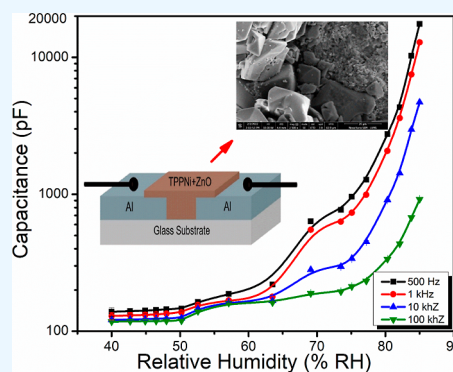
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ABSTRACT: The development of high-performance humidity sensors to cater for a plethora of applications, ranging from agriculture to intelligent medical monitoring systems, calls for the selection of a reliable and ultrasensitive sensing material. A simplistic device architecture, robust quantification of ambient relative humidity (% RH), and compatibility with the contemporary integrated circuit technology make a bimodal (capacitive and resistive) surface-type sensor to be a prominent choice for device fabrication. Herein, we have proposed and demonstrated a facile realization of a 5,10,15,20-tetraphenylporphyrinatonicel (II)–zinc oxide (TPPNI–ZnO) nanocomposite-based bimodal surface-type % RH sensor. The TPPNI macromolecule and ZnO nanoparticles have been synthesized by an eco-benign microwave-assisted technique and a thermal-budget chemical precipitation method, respectively. It is speculated from the morphological study that specific surface area improvement, via the provision of ZnO nanoparticles on micro-pyramidal structures of TPPNI, may reinforce the sensing properties of the fabricated humidity sensor. The relative humidity sensing capacitive and resistive characteristics of the sensor have been monitored in 40–85% relative humidity (% RH) bandwidth. The fabricated sensor under the biasing conditions of 1 V of applied bias (V_{rms}) and 500 Hz AC test frequency exhibits a significantly higher sensitivity of 387.03 pF/% RH and 95.79 k Ω / % RH in bimodal operation. The average values of both the response and recovery times of the capacitive sensor have been estimated to be $\sim$ 30 s. It has also been debated why this high degree of sensitivity and considerable reduction in response/recovery time has been obtained. In addition, the intense and wide bandwidth spectral response of the TPPNI–ZnO nanocomposite indicates that it may also be utilized as a potential light-harvesting heterostructured nanohybrid in future studies.



1. INTRODUCTION

The reliable, ultrasensitive, and robust quantification of ambient relative humidity is highly desirable in numerous sectors related to our daily life, such as agriculture, smart homes, intelligent medical monitors, pharmaceuticals, and so on.¹ The humidity level in the respiration effectively reflects the human metabolism and health;² in fact, the extreme conditions of humidity are known to have adverse effects on human health and may be linked to several diseases.³ Similarly, ambient relative humidity plays a pivotal role in photosynthesis, transpiration, and temperature regulations in plants. Therefore, to ensure a high growth rate of plants/crops and enriched agricultural productivity, the measurement and analysis of the water status of plants (in real time) are of utmost importance.⁴ Driven by this plethora of applications, there has been extensive development of precise and high-performance humidity sensors lately.⁵

Recently, (a) various novel transduction mechanisms and (b) active sensing layers exhibiting unique physiochemical properties have been adopted for humidity sensors to achieve superior sensitivity, a robust response/recovery time, a wide relative humidity working range, a higher order of linearity in response, and facile reading out of electrical output signals.⁶ Owing to the simple structure, ease of device fabrication, being inexpensive, compatibility with the contemporary integrated circuit (IC) technology and the possibility of smart sensor applications, a bimodal (capacitive and resistive) surface-type sensor is the natural choice for relative humidity sensing.⁷ The

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material selection for the active sensing layer of the humidity sensors is the major facet; consequently, various research and development efforts have been devoted to exploring novel humidity sensing scaffolds.⁸ Researchers have developed various materials for humidity sensing including metal oxides, ceramics, carbon materials, perovskites, polymers, and composites.⁹ Organic semiconductors/polymers, in particular, have drawn increasing interest because of their varied architectures, flexible nature and stretchability, adjustable and changeable performance, and inexpensive cost.¹⁰ Organic semiconductors for humidity detecting applications, however, must meet specific criteria, including hydrophilicity, exceptional porosity, and the sensing layer's capacity to be insoluble in water.^{6d}

K. Rehman et al. recently investigated a capacitive humidity sensor using tris(8-hydroxyquinoline) gallium (GaQ₃) nanofibers and reported a sensitivity of 70 pF/% RH.¹¹ Andika et al. studied a new nanoporous structure of aluminum 1,8,15,22-tetrakis 29H,31H phthalocyanine chloride (AlPcCl) humidity-sensitive film produced using the anodic aluminum oxide (AAO) template and found that it had a sensitivity of 72 fF/% RH.¹² A novel type of humidity-sensitive material based on 5,10,15,20-tetraphenylporphyrinatonicel (II) (TPPNI) macromolecules was recently reported by our group. Both the resistance and capacitance of the TPPNI macromolecule-based humidity sensor exhibited reasonably good sensitivity (146.17 pF/% RH at 500 Hz and 48.23 k Ω /RH at 1 kHz) in response to variation in % RH, between 39 and 85%.¹³ Due to the slow response/recovery time (130 s/156 s), the TPPNI-based humidity sensor, however, may not be suited for respiratory monitoring. To satisfy the rigorous criteria, we propose that the sensitivity, stability, and response time of the TPPNI-based humidity sensor should be further improved by metal oxide nanostructure doping.

Zinc oxide (ZnO) is a potential n-type II-VI semiconductor with exceptional optical and electronic properties. Bulk ZnO is a direct band gap, wurtzite-type, and thermodynamically stable semiconductor with an energy band gap (E_g) of ~ 3.37 eV at 300 K and an exciton binding energy of 0.060 eV.¹⁴ At ambient temperature, the electron mobility in ZnO has been demonstrated to be as high as 100 cm²/Vs, which is many orders of magnitude greater than that observed in organic semiconductors.¹⁵ Furthermore, the unique morphologies exhibited by zinc oxide nanostructures also make them ideal for humidity sensing applications. Interestingly, the interplay between optical, electronic, and chemical properties of organic/inorganic (porphyrins and ZnO) nanocomposites may give rise to a novel category of the humidity sensing matrix.¹⁶ Another benefit of utilizing ZnO as a composite moiety in the sensing layer is the reduction or elimination of the water solubility, which enhances the stability of the humidity sensing device.¹⁷

Various studies have also proved that the sensing performance of the organic devices may be effectively enhanced by the addition of inorganic guest components into the organic host framework to form novel nanocomposites with synergetic or complementary behaviors (considering the possibility to combine the advantages of organic and inorganic counterparts).¹⁸ Typically, the composite materials consist of two or more constituents intermixed at the molecular level to seek synergistic advantages from the collective set of individual physicochemical properties.¹⁹ In the past, exploiting the synergistic combination of materials, the performance of

various electronic devices (including humidity sensors) has already been significantly improved. For instance, Z.X. Xu et al. revealed that incorporation of ZnO nanomaterials into the polymer (MEH-PPV) matrix enhances the mobility of the organic field-effect transistor (OFET) devices by up to 3 orders of magnitude.²⁰ We believe that the emergence of charge-transfer complexes, generation of more oxygen vacancies,²¹ inhibition of degradative intermolecular self-reactions,²² and reactivity enhancement due to the improved effective surface area in the TPPNI-ZnO nanocomposite make it a promising heterogeneous active scaffold for humidity sensing applications.

In the present work, we hereby propose and demonstrate a facile realization of a 5,10,15,20-tetraphenylporphyrinatonicel (II)-zinc oxide nanocomposite-based bimodal relative humidity sensor. The sensing properties, including capacitive and resistive sensitivity, bandwidth, and response-recovery time, have been investigated. The sensing mechanism of the fabricated sensor has also been analyzed according to the experimental data.

2. EXPERIMENTAL SECTION

2.1. Synthesis of TPPNI Macromolecules. In two sequential phases, the TPPNI macromolecule has been prepared. In the initial phase of the process, the condensation of pyrrole and benzaldehyde has been conducted to get 5,10,15,20-tetraphenylporphyrin (TPP).²³ A combination of benzaldehyde (0.05 mmole, 4.25 g) and pyrrole (0.04 mmole, 2.68 mg) has been adsorbed into the acidified silica gel (5.0 g) using microwaves (200 W) at 100 °C for 6 min. After purification, utilizing column chromatography over silica gel with chloroform and *n*-hexane (2:1) as eluents, a 24% free base porphyrin (TPP) chemical was obtained. After dissolving nickel acetate (1 mmole, 176.78 mg) and TPP (0.04 mol, 24.56 mg) in a 1:10 mixture of methanol and chloroform, the compound was adsorbed onto silica gel in the second step. After drying, microwave irradiation (250 Watts) has been applied to silica gel at a temperature of 111 °C for 15 min. The reaction mixture was put on the top of a silica column and eluted with a combination of chloroform and *n*-hexane (1:4) after cooling. The fast-moving band has been collected, and the solvent has been evaporated in vacuo to afford the pure 5,10,15,20-tetraphenylporphyrinatonicel (II) in 91% yield.

2.2. Synthesis of ZnO Nanoparticles. In the present study, zinc oxide nanoparticles have been synthesized by the chemical precipitation method. 99% pure zinc nitrate Zn(NO₃)₂·6H₂O has been utilized as the starting material, which has been purchased from Dukson (Korea), and has been used as received without any further purification. Primarily, 1 M solution of zinc nitrate has been prepared in deionized water (DIW) and stirred vigorously for 30 min at 100 °C for effective dissolution. Similarly, 1 M sodium hydroxide (NaOH) solution in DIW has also been prepared separately and subjected to 30 min of constant stirring at room temperature. Later, NaOH solution was added dropwise in zinc nitrate solution until the pH of the resulting solution reached 12, and the solution eventually became milky. The milky solution was left unattended so that zinc oxide particles may settle down as precipitates. The precipitates have been later filtered by using filter paper and washed several times with DIW. The resulting ZnO particles were collected in a Petri dish and heated in an oven overnight at ~ 300 °C. Zinc oxide particles were later

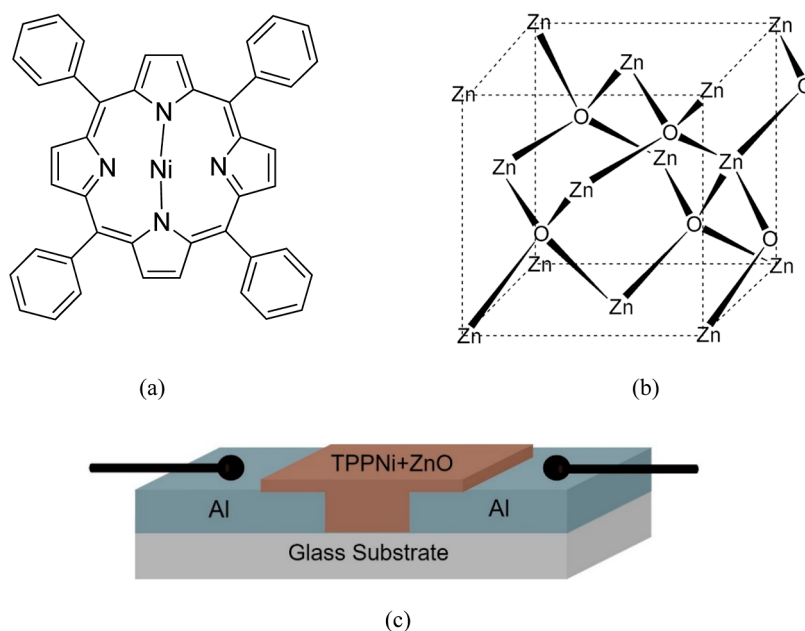


Figure 1. Chemical structure of (a) 5,10,15,20-tetraphenylporphyrinatonicel (II) macromolecule (TPPNi) and (b) zinc oxide nanoparticles and (c) schematic illustration of the TPPNi-ZnO nanocomposite-based bimodal humidity sensor.

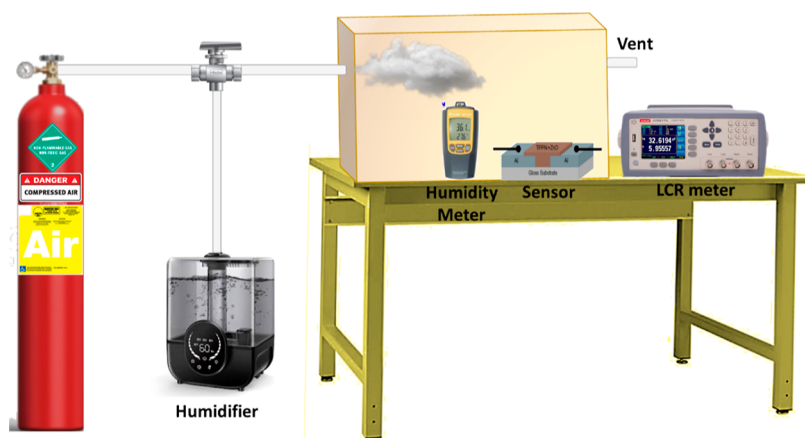


Figure 2. Schematic diagram of the characterization setup used for the Al/TPPNi-ZnO/Al bimodal humidity sensor.

finely grounded via a mortar and pestle to obtain ZnO nanoparticles.

2.3. Fabrication of the Humidity Sensor. A planar and surface-type design was used to create the bi-modal relative humidity sensor. To serve as a stiff substrate for the fabrication of a bimodal humidity sensor, commonly used soda lime microscopic glass slides with $\sim 25 \times 25 \times 1$ mm dimensions were used. In the first stage, the substrate slides have been meticulously scrubbed using a cotton cloth piece soaked in soap water. The scrubbing of slides has been performed following a pre-defined and well-established ultrasonic cleaning protocol using an ultrasonic cleaner (model: Elma sonic E 30H), that is, rinsing in soap water, followed by DIW and cleaning with acetone, ethanol, and DI water for 5 min each. Finally, the substrate glass slides were dried under dust-free conditions using a compressed dry air blow.

After that, using the specially constructed physical vapor deposition (PVD) system with a deposition rate ~ 0.2 nm/s, a thin layer of aluminum metal (thickness ~ 120 nm) was deposited on precleaned glass substrates. In the construction of

the aforementioned PVD system, a diffusion pump (model: VHS-4 - Agilent Technologies, pumping speed 750 L/s) backed with a single-stage rotary vane pump (model: Hena25 - Pfeiffer, pumping speed 25 m³/h) has been utilized to evacuate the chamber to a required vacuum of 1×10^{-5} mbarr. A wire shadow mask was used to create a ~ 40 μ m gap between the two aluminum electrodes. The metallic electrodes thus formed will later serve the purpose of electrical contact pads during the electrical characterization of the bimodal humidity sensor. In the later stage of humidity sensor fabrication, the separation between the metallic electrodes has been covered with the TPPNi-ZnO nanocomposite. For this purpose, 15 mg/ml TPPNi solution has been prepared in chloroform and 5 wt % ZnO doping of this solution has been realized. The resulting nanocomposite solution has been stirred overnight for complete dissolution. The drop-casted thin film of the TPPNi-ZnO nanocomposite (thickness ~ 150 nm) between the metallic electrodes serves the purpose of the humidity sensing dielectric thin film. Figure 1a,b represents the chemical structure of the TPPNi macromolecule and ZnO, respectively.

However, the cross-section of the bimodal humidity sensor is displayed in Figure 1c below.

2.4. Sensor Testing. Sensing performance evaluation of the bimodal humidity sensor has been performed in a laboratory-built (hermetically sealed) box. Dry and humid airflow within the environmental chamber has been regulated by input and output regulation valves to adjust/control the relative humidity within the humidity chamber. During the whole experimental work, the variation of temperature and humidity within the humidity chamber has been repetitively monitored after regular intervals using a hygrometer (Model: Pro skit MT 4014). The hygrometer used in the present study offers a humidity resolution as low as $\sim 0.1\%$ RH and a resolution in temperature monitoring of $\sim 0.1^\circ\text{C}$.

The high-accuracy LCR meter (model: APPLANT AT2816B) with a measurement accuracy of 0.1% has been utilized for electrical characterization of the bimodal humidity sensor. Specifically, during the electrical characterization, the capacitance and resistance of the fabricated bimodal humidity sensor have been monitored at various humidity levels. For electrical characterization, the input AC signal has been set at different frequency values (500 Hz, 1, 10, and 100 kHz). In contrast, the applied voltage has been fixed at 1.0 V. Figure 2, given below, demonstrates the whole electrical characterization testing setup utilized in our present study.

In the present study, the GENESYS 10S UV–vis spectrophotometer has been used to study the optical properties of TPPNi, ZnO, and their nanocomposite. The humidity sensing layer has been examined using an FESEM “Nova Nano SEM 450 Field-Emission Scanning Electron Microscope” to investigate its surface morphology. Further, the X-ray diffraction (XRD) pattern of the active sensing layer and its constituents has been recorded using a Shimadzu 7000 Diffractometer functioning with Cu K α 1 radiation ($\lambda = 0.15406\text{ nm}$) generated at 30 kV and 30 mA with a scan rate of 2° min^{-1} for 2θ values between 15 and 75° .

3. RESULTS AND DISCUSSION

The photophysical properties of the humidity sensing active layer (TPPNi-ZnO) have been studied in the wavelength range of 350–800 nm using UV–vis absorption spectroscopy. Specifically, Figure 3 represents the absorption spectrum of the TPPNi-ZnO nanocomposite-based thin film. Figure 3 (inset) represents the solid-state and solution-state (aqueous) absorption spectra of TPPNi and ZnO nanoparticles, respectively.

It is well understood that the absorption spectrum of porphyrin exhibits two electronic transitions, namely, Soret (S)-band and Q-band at roughly 350–500 and 500–700 nm, respectively.²⁴ The typical Soret band was observed between 370 and 515 nm in the solid-state absorption spectra of TPPNi, with a peak absorption at (max 473.5 nm), which is attributable to the $\pi\text{--}\pi^*$ transition from the ground state (S_0) to the second-lowest singlet state (S_2). However, the Q-band in the 525–700 nm wavelength range is due to $\pi\text{--}\pi^*$ electron transition from the ground state (S_0) to the lowest excited singlet state (S_1). Further, zinc oxide’s solution-state absorption spectrum indicates its maximum absorption at ($\lambda_{\text{max}} \sim 365\text{ nm}$). Figure 3 portrays that the TPPNi-ZnO thin film exhibits maximum absorption at 435 nm. Interestingly, with the inlay of ZnO nanoparticles in the TPPNi matrix, the characteristic S-band peak of the TPPNi-ZnO nanocomposite exhibits a 38.5 nm hypsochromic shift (blue shift) and a

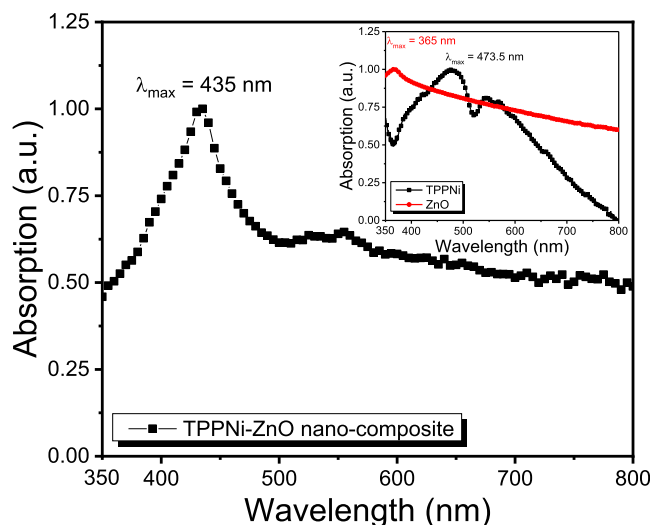


Figure 3. Absorption spectrum of the TPPNi-ZnO nanocomposite-based thin film and (inset) solid-state and solution-state (aqueous) absorption spectra of pristine TPPNi and ZnO in the UV–vis range, respectively.

weaker intensity of the Q-band in the absorption spectrum, thereby confirming the formation of the TPPNi-ZnO nanocomposite.²⁵ The intense and wide bandwidth spectral response of the TPPNi-ZnO nanocomposite indicates that in future studies, it may be utilized as a potential light-harvesting heterostructured nanohybrid.

Figure 4 depicts the relation of diffraction intensity as a function of angle (2θ) for TPPNi, ZnO, and TPPNi-ZnO

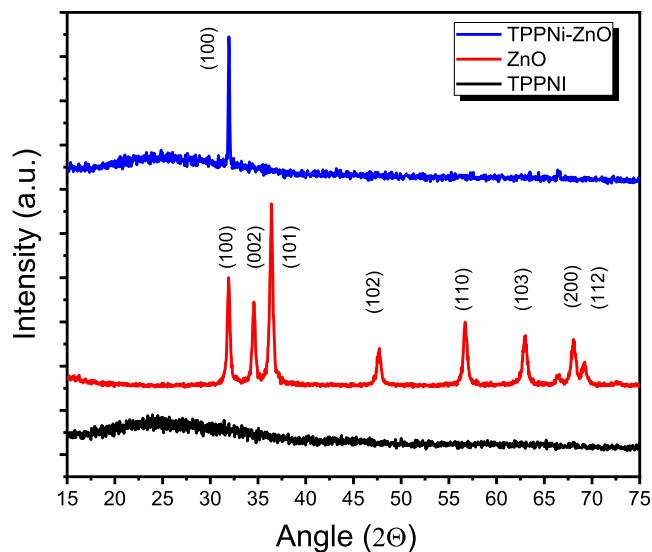


Figure 4. XRD spectra of the TPPNi thin film, zinc oxide powder, and TPPNi-ZnO nanocomposite thin film.

nanocomposite thin films. The XRD profiles have been examined in the range of $2\theta = 15\text{--}75^\circ$ to study the crystalline structure of all three samples. In the case of the TPPNi thin film, first the absence of any distinct characteristic XRD peaks and secondly the presence of a broad “halo” pattern at $2\theta = 23.5^\circ$ confirm the amorphous, glassy, or disordered structure.²⁶ In the case of the ZnO powder sample, the strong and narrow peaks at $2\theta = 31.88, 34.48, 36.44, 47.64, 56.68, 62.92, 67.96,$

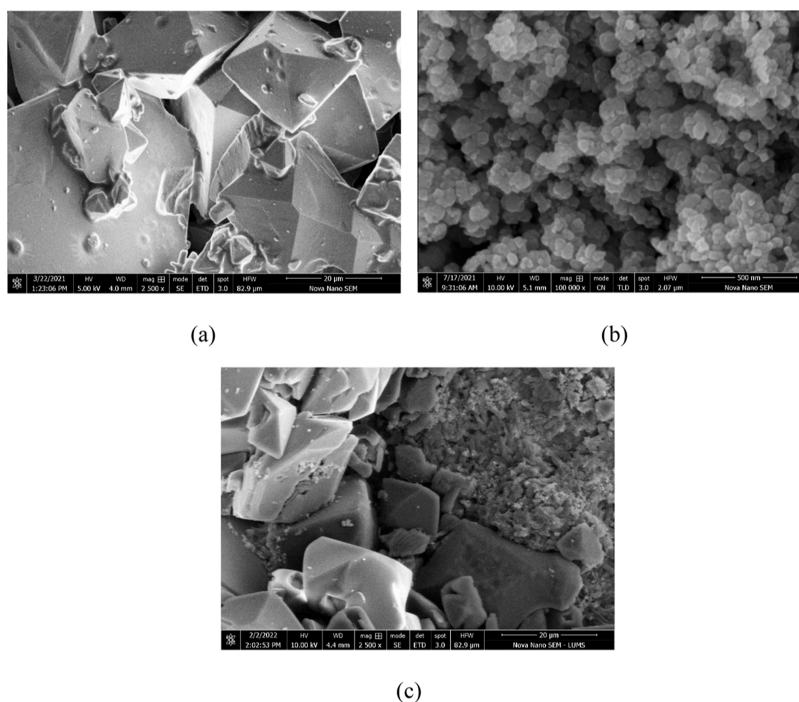


Figure 5. FESEM micrographs of (a) TPPNi thin film at 2.5kX, (b) zinc oxide nanoparticles at 100kX, and (c) TPPNi-ZnO nanocomposite at 2.5kX magnification scale.

and 69.16° indicate the good crystalline (hexagonal wurtzite) structure of synthesized ZnO nanostructures (JCPDS card no.: 00-036-1451).²⁷ Finally, for the TPPNi-ZnO nanocomposite thin film, both (a) a halo pattern at $2\theta = 23.5^\circ$ and (b) a sharp signature intense peak at $2\theta = 31.88^\circ$ have been observed, which may safely be attributed to TPPNi and ZnO constituents, respectively. The absence of other relatively non-significant peaks of ZnO in the XRD profile may be due to less doping concentration of ZnO in the TPPNi-ZnO nanocomposite.

To investigate the surface morphology of the constituents of the humidity sensing layer (TPPNi-ZnO nanocomposite), field emission scanning electron microscopy (FESEM) analysis has been performed. Figure 5 portrays the FESEM micrographs of (a) the pristine TPPNi thin film, (b) ZnO nanoparticles, and (c) TPPNi-ZnO nanocomposites at 2.5, 100, and 2.5 k magnification scales, respectively. It is observed that the pristine TPPNi thin film comprises micro-pyramidal-shaped structures with essential voids in between. Hence, the pristine TPPNi thin film's internal bulk comprises micropores/voids, which interestingly form an interconnected network (from the film surface to the substrate), much like a spongy structure. The spongy structure of the pristine TPPNi thin film is beneficial for the superior humidity sensing performance of the device since it ensures adequate humidity circulation through the bulk. It may be observed from Figure 5c that incorporating ZnO nanoparticles (average size ~ 100 nm) on the pyramid-shaped TPPNi microstructures has yielded a significantly high specific area for enhanced humidity adsorption on the active layer. Hence, in the present study, we have investigated the humidity sensing capability of the TPPNi-ZnO nanocomposite-based active layer.

Humidity affects the various chemical, physical, and biological processes, so humidity sensors generally rely on the processes mentioned above to estimate the fluctuation in

ambient moisture levels.²⁸ Here in this study, the sensing layer of TPPNi-ZnO works as a dielectric material when the humidity sensor is operated in the capacitive mode. In response to the changes in environmental relative humidity, the active TPPNi-ZnO nanocomposite layer absorbs/desorbs water, altering the capacitance of the sensor. The capacitance of such a humidity sensor depends on various parameters, mathematically expressed in eq 1²⁹

$$C = \frac{\epsilon_r A}{4\pi k d} \quad (1)$$

where “C” refers to the capacitance of the fabricated humidity sensor, “A” refers to the total area of the metallic electrodes, “d” denotes the interelectrode distance, “k” is the electrostatic force constant, and “ ϵ_r ” denotes the dielectric permittivity of the humidity sensing material (i.e., TPPNi-ZnO nanocomposite).

Due to the occurrence of polarization in the humidity sensing layer (TPPNi-ZnO), the dielectric permittivity increases. Four mechanisms may be involved in sensing layer polarizability, that is, dipolar, ionic, space charge, or electronic.³⁰ The given equation (eq 2), named Clausius–Mosotti equation, expresses the relationship between materials relative constant (ϵ_r) and polarizability (α_d)³¹

$$\epsilon_r = \left(\frac{(1 + 2N_d \alpha_d)/3\epsilon_0}{(1 - N_d \alpha_d)/3\epsilon_0} \right) \quad (2)$$

eq 3 describes the relationship between dielectric constant and capacitance³²

$$\frac{C_S}{C_0} = \left(\frac{\epsilon_{\text{wet}}}{\epsilon_{\text{dry}}} \right)^n = \left(\frac{(1 + 2N_w \alpha_w)/3\epsilon_0}{(1 - N_w \alpha_w/3\epsilon_0)\epsilon_{\text{dry}}} \right)^n \quad (3)$$

In this case, ϵ_{dry} and ϵ_{wet} are the relative dielectric permittivity constants of dry and moist active sensor layers,

respectively, and “ n ” is associated with the sensing layer surface morphology. In general, the ϵ_{dry} for the dried organic semiconductor layer is ~ 5 , which is significantly lower than the dielectric permittivity of water ($\epsilon_{\text{water}} \sim 80$). As water molecules continue to be absorbed by the TPPNi-ZnO active sensing layer, the humid sensing layer's dielectric permittivity increases significantly.³³

Excitingly, the organic semiconductor-based sensors, operated in the capacitive mode, provide remarkably high selectivity, in particular toward relative humidity sensing. Evidently, from the simple closed-form mathematical expression (eq 1), the detection principle of capacitive sensors demands a mandatory change in “ ϵ_r ”, “ A ”, or “ d ” of the sensor to effectively sense the analyte chemical species/gas molecules. Since “ A ” and “ d ” relate to the geometry of the sensor and often remain invariant during the sensing process, the major possibility to observe a drastic variation in capacitance is by generating a notable change in the dielectric permittivity of the sensing film after the adsorption of analyte molecules. Hagleitner et al. have previously confirmed that the capacitance of a sensing device is only increased if the dielectric permittivity of the analyte molecules physisorbed in the sensing matrix volume is considerably higher.³⁴ However, it is well understood that the dielectric permittivity of vacuum is exactly unity, whereas for notable gases (e.g., NH_3 , CO , CO_2 , N_2O , and CH_4), it is close to unity.³⁵ Similarly, the dielectric permittivity of common chemical analytes is also significantly smaller as compared to that of water molecules (~ 80).³⁶ For instance, the dielectric permittivity of toluene, n -octane, and 1-propanol is 1.89, 2.38, and 1.95, respectively.³⁷ The changes in dielectric constant due to the interaction between the active sensing layer and notable chemical analytes/gases molecules are therefore highly implausible.

Admittedly, on the other hand, metal oxide gas sensors have shown exceptionally high sensitivity to many chemicals and gases. Therefore, one may argue that the introduction of ZnO metal oxide in the organic semiconductor host may cause cross-sensitivity of gases instead. However, it must be undermined that the three key processes occurring on the ZnO surface during the gas sensing mechanism are adsorption, desorption, and activity of the O^- ions.³⁸ All these processes are highly dependent upon temperature, and therefore, metal oxide-based gas sensors are usually operated at high temperatures. For instance, the formation of O^- in metal oxides is favored at temperatures between 150 and 300 $^\circ\text{C}$,³⁹ whereas in the present study, the sensor has been operated for humidity sensing applications at room temperature.

In the present study, the electrical characteristics of the fabricated thin film humidity sensor have been measured in the AC field. Figure 6 displays the capacitance versus % RH response of the fabricated sensor for the range of % RH from 40 to 85% at four diverse AC test signal frequencies (i.e., 500 Hz, 1, 10, and 100 kHz). For all test frequencies, the capacitance of the fabricated sensor exhibits a quasi-linear increase as a function of % RH. At 500 Hz AC test frequency, with varying % RH from 40 to 85%, the capacitance of the fabricated sensor increased by a magnitude of 126.66 times in magnitude. The comparative variation in the device's capacitance (for the same % RH variation) at higher test frequencies is significantly lower. Specifically, the capacitance variation has been observed to be 99.95 times at 1 kHz, 38.81 times at 10 kHz, and 7.82 times at 100 kHz. Consequently, the fabricated device's humidity sensitivity has been determined to

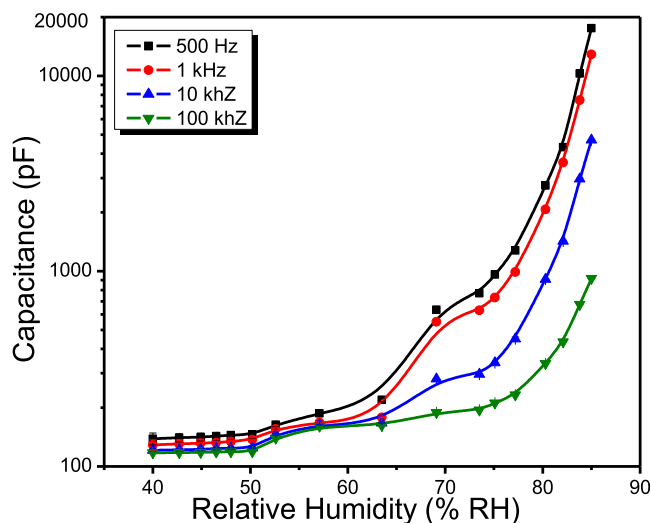


Figure 6. Effect of selected bias frequency on capacitance vs % RH characteristics of the Al/TPPNi-ZnO/Al humidity sensor (the error bar is too small to be visible on the linear scale).

be 387.03, 283.69, 101.64, and 17.79 pF/% RH at varied test frequencies, that is, 500 Hz, 1, 10, and 100 kHz, respectively. Thereby, the sensitivity of the humidity sensor has been calculated as follows (eq 4)⁴⁰

$$\text{Sensitivity} = \frac{\Delta C}{\Delta(\% \text{ RH})} \quad (4)$$

As a result of this, two observations are particularly noteworthy. First, albeit for an ideal capacitor, the capacitance value is generally independent of applied AC test frequency.⁴¹ However, remarkably in our present study, for a lower operating frequency (i.e., 500 Hz), the effect of % RH variations on device capacitance is more significant than those observed for higher AC test frequencies. The humidity–capacitance sensing properties of the humidity sensor are considerably affected by the measurement frequencies, according to Islam et al.⁴²

It may be observed that the sensor has a relatively nonlinear response, where the sensitivity has typically increased with an increase in humidity. Chappanda et al. have previously claimed that such behavior signifies that the amount of water absorbed at equilibrium by the sensing material increases nonlinearly with an increase in % RH.⁴³ Resultantly, the sensor response at high % RH masks the response at low % RH, creating two distinct regions. Admittedly, from Figure 6, it may be witnessed that the capacitance increases more rapidly in the high % RH range (60–85%) as compared to the lower one (~ 40 to 60%). In fact, in the low % RH range, water molecules are initially chemisorbed (in the form of a monolayer) on the active thin film due to intermolecular interactions.^{17,44} Hence, at this stage, in the chemisorbed water molecule layer, the electron tunneling phenomenon between OH^- or H_2O molecules is primarily responsible for the detection of low humidity.⁴⁵ However, in the case of high ambient % RH environments, multi-physisorbed water molecule layers tend to form on the pre-deposited chemisorbed monolayer of water molecules.⁴⁶ At this stage, (a) the higher mobility in the multiple physisorbed layers and (b) the self-dissociation of water molecules dominate, which favor the higher conductivity owing to proton donation between water molecules.⁴⁷

Consequently, with the absorption of more water molecules, the active layer further exhibits leak conduction (γ).⁴⁸ The capacitance (C) of the humidity sensor exhibiting leak conduction may thus be expressed by the following mathematical relation⁴⁹

$$C = \varepsilon^* C_0 = \left(\varepsilon_r - \frac{i\gamma}{\omega \varepsilon_0} \right) C_0 \quad (5)$$

Here, ε^* and C_0 represent the complex dielectric permittivity and capacitance for the ideal situation, respectively (low % RH), whereas γ , ω , and ε_0 represent the leak conductance, angular frequency, and dielectric permittivity of free space, respectively. It may be easily inferred from eq 5 that the capacitance of the humidity sensor is directly related to the leak conductance " γ " and inversely related to the angular frequency " ω " of the AC test signal. The mathematical expression serves to explain the two observations above easily.

Interestingly, the organic semiconductor–metal oxide nanocomposites have a technologically appealing charge-transfer characteristic that is significantly influenced by environmental circumstances, particularly humidity. Figure 7 displays the

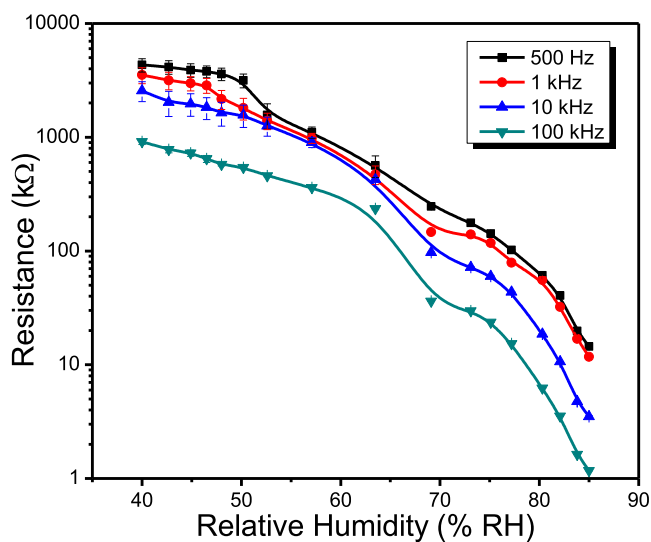


Figure 7. Effect of applied frequency on resistance vs % RH characteristics of the Al/TPPNi-ZnO/Al humidity sensor.

impact of ambient relative humidity on the resistance of the fabricated sensor. The results portray the resistive-relative humidity response in the 40–85% RH range for different test frequencies (500 Hz, 1, 10, and 100 kHz). It is easy to notice that the sensor's resistance follows a consistent and similar trend across all test frequencies; that is, as the % RH increases, the magnitude of resistance decreases in a quasi-linear fashion. At a 500 Hz test frequency, an electrical resistance increase of ~ 299.10 times is registered at 85% RH compared to 40% RH, yielding a sensitivity of 95.79 k Ω / % RH. Similarly, the sensitivity at 1 kHz, 10, and 100 kHz has been measured to be 78.02, 56.92, and 20.25 k Ω / % RH, respectively. The aforementioned outcomes show that the TPPNi-ZnO nanocomposite-based humidity sensor can successfully work as a bimodal sensor (i.e., a resistive and capacitive sensor) for ambient relative humidity assessment.

The Grothus mechanism (proton hopping) may be used to describe the operation of resistive-type sensors. On the surface

of a TPPNi-ZnO nanocomposite thin film, predominantly stationary chemisorbed water molecules occur at a low RH range, and in this stage, the conduction in the active layer is mainly because of intrinsic electrons.⁵⁰ As the % RH level is gradually raised, the active surface will be shielded by multilayers of the physisorbed water molecule. These physisorbed layers have liquid-like behavior and quickly break down into hydronium ions (H_3O^+) (as expressed by chemical eq 6). Therefore, at higher % RH, ions are responsible for conduction in the sensing film.⁵¹ The bulk of hydronium ions (H_3O^+) gives hydrogen ions (H^+) to the neighboring adsorbed water molecule. The chain reaction will continue in this manner. The electrical impedance of the active sensing layer is considerably reduced by efficient proton hopping between adjacent molecules in physisorbed H_2O molecular layers.⁵² Interestingly, since the interaction force between the polar ZnO surface and polar molecules (like water) is relatively stronger, the introduction of ZnO nanoparticles to the surface of TPPNi dielectric can increase the number of water molecules absorbed on the resulting TPPNi-ZnO composite humidity sensing layer.⁵³ The adsorption of water molecules produces ions, and subsequent dissociation of H_2O molecules causes efficient directional charge conduction within the TPPNi-ZnO nanocomposite by virtue of the inherent p–n junction at the TPPNi and ZnO interface



The effect of temperature on output characteristics of the humidity sensor has also been studied. The capacitance value of the humidity sensor (when operated at 100 kHz frequency) has been observed to increase by around 6.1% with a progressive increase in temperature from 25 to 75 °C. In general, with the increase in temperature, the resistance and capacitance of the humidity sensors decrease and increase, respectively.⁵⁴ It is noteworthy that the capacitive and resistive response of the sensor presented in this study is the average experimental result of two humidity sensing devices fabricated under identical fabrication conditions. The average fluctuation in experimental results is already presented in terms of error bars. To investigate the long-term stability, the sensor was stored under the ambient conditions for 2 months and the average decrease in capacitive sensitivity was estimated within 5.3% at 500 Hz and 3.1% range at 100 kHz operational frequency. These results reveal that there is no significant drift in the aging process of the humidity sensing device, which validates that the fabricated humidity sensor satisfies the long-term stability requirement.

It is well understood that the superior response and recovery times are vital in evaluating the sensing performance of the sensors. The sensor's transient, capacitive, and resistive responses to step input between low (45%) and high (85%) ambient % RH values are depicted in Figure 8a,b. It is pertinent to mention that the response time is defined as the time required for the capacitive humidity sensor to accomplish 90% of the saturated capacitance value across the high % RH region; similarly, the recovery time is defined as the time required by capacitance of the device to alter from a local maximum to within 10% of the average minimum value across the low % RH region.⁵⁵ From Figure 8a, it is observed that at constant 45% RH value, the response is quite stable up to 50 s for TPPNi-ZnO nanocomposite-based capacitive sensors but increases to its maximum with an average response time of

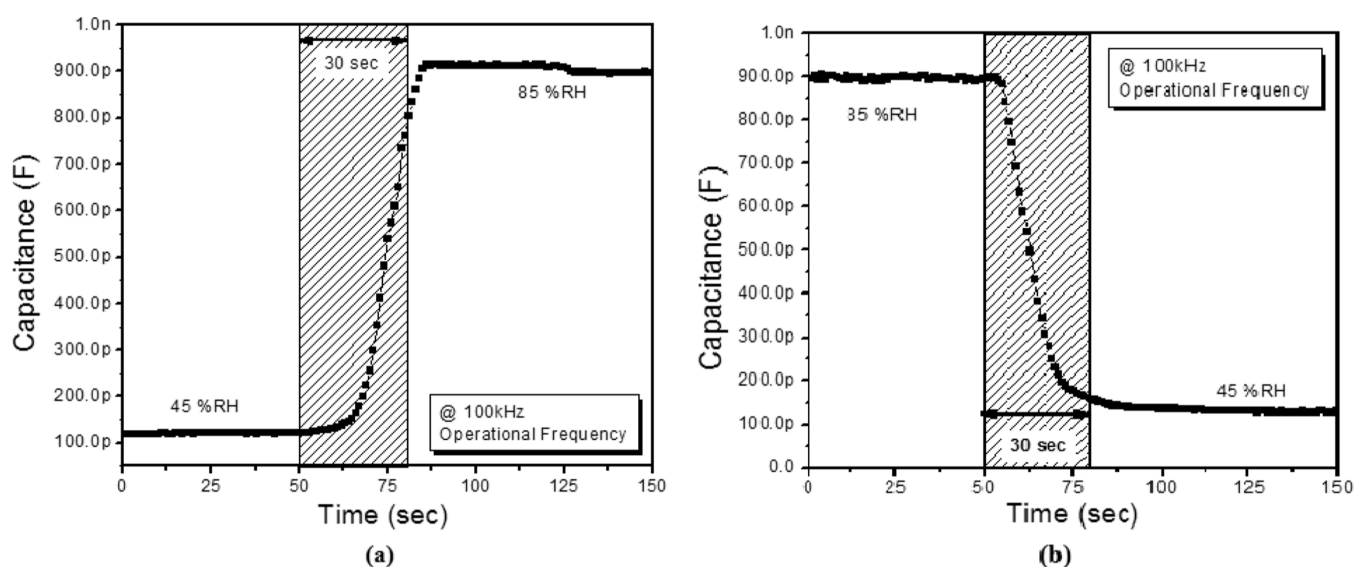


Figure 8. Response (a) and recovery (b) time estimation at 100 kHz measured by applying the step change in % RH from 45 to 85% and from 85 to 45% RH, respectively.

Table 1. Assessment of Humidity Sensors Based on Key Performance Considerations

material	mode of operation	bandwidth	sensitivity	response/ reset time
nanofibers of tris(8-hydroxyquinoline) gallium (Gaq3) ¹¹	capacitive	35–75 % RH	70 pF/% RH @ 1kHz	6 s each
nanostructured aluminum 1,8,15,22-tetrakis 29H, 31H phthalocyanine chloride (AlPcCl) ¹²	capacitive	20–90 % RH	72 fF/% RH @ 1kHz	
2-aminoanthraquinone (AAQ) ^{5b}	capacitive	40–88 % RH	0.4 pF/% RH @ 120 Hz	19, 25 s
ITO/PTB7- Th/PCBM/graphene composite ⁵⁶	capacitive	50–93 % RH	1731 pF/% RH	16, 52 s
microporous zinc phthalocyanine (ZnPc) ⁵⁷	capacitive	20–100 % RH	1.03 pF/% RH	15, 10 s
methyl-red ⁵⁸	capacitive	30–95 % RH	16.92 pF/% RH	~10 s each
TPPNi ¹³ (control sample)	capacitive and conductometric	39–85 % RH	48.23 kΩ/% RH @ 1kHz	130, 156 s
TPPNi–ZnO nanocomposite (present work)	capacitive and resistive	40–85 % RH	95.79 kΩ/% RH @ 500 Hz	30 s each

~30 s when % RH changes from 45 to 85%. Likewise, the recovery time of the proposed humidity sensor (in the capacitive mode) has been evaluated to be ~30 s, as depicted in Figure 8b. In general, the fabricated humidity sensor's relatively quicker response/recovery time may safely be ascribed to the effective diffusivity of water molecules and improved charge carrier mobility in the active sensing layer. It is pertinent to mention that it may be observed from Figures 6 and 7 that the fabricated humidity sensor shows superior stability in its response at a higher order of operational frequency, so the higher frequency (100 kHz) has been judiciously selected as an optimized frequency for estimating the response/recovery of the humidity sensor.

In terms of important performance parameters, Table 1 compares the proposed TPPNi–ZnO nanocomposite-based integrated capacitive- and resistive-type humidity sensor to previously reported sensors. In general, the enhancement in the sensing performance of the fabricated humidity sensor may be attributed to the p–n heterojunction formed by TPPNi macromolecules and ZnO nanoparticles.

4. CONCLUSIONS

In this research, the quest for the development of precise and high-performance humidity sensors to serve a wide range from Industry 4.0 to Smart City applications has been catered by selecting an appropriate material for reliable, ultrasensitive, and

robust quantification of ambient relative humidity. In this work, we have successfully presented fabrication and characterization of 5,10,15,20-tetraphenylporphyrinatonicel (II)–Zinc oxide (TPPNi–ZnO) nanocomposite-based thin films for their use as a surface type relative humidity sensor. To realize this, TPPNi macromolecules have been synthesized by a microwave-assisted technique and nanoparticles of ZnO have been synthesized by the chemical precipitation method. The fabricated bimodal relative humidity sensor (Al/TPPNi–ZnO/Al) has a layer structure consisting of thermally deposited aluminum (Al) thin film (~120 nm) planar electrodes separated by a gap of 40 μm (created by the shadow mask process) and deposition of the TPPNi–ZnO nanocomposite as an active layer by drop-casting.

The photophysical characterization study has been performed, which confirms the formation of the TPPNi–ZnO nanocomposite. According to the XRD study, the TPPNi–ZnO nanocomposite thin film has shown both a halo pattern at $2\theta = 23.5^\circ$ and a sharp signature intense peak at $2\theta = 31.88^\circ$, reflecting the presence of TPPNi and ZnO constituents. Further, the surface morphology has been investigated with the help of FESEM, and it has been observed that the TPPNi thin film depicts a spongy structure and ZnO is like nanoparticles and the combination of nanocomposites of TPPNi–ZnO is assumed to increase the effective surface area of the sensing layer.

In the present study, the capacitive and resistive characteristics of the proposed humidity sensor have been evaluated in the 40–85 % RH bandwidth at four diverse AC test signal frequencies. Specifically, the electrical characterization shows an increase of 164.78% in capacitive response and 98.61% in resistive response along with a considerable decrease in the response and recovery times, as compared to the control TPPNi-based humidity sensor. The provision of ZnO nanoparticles on pyramidal structures of TPPNi thin films is speculated to be one of the reasons due to which an increase in the sensitivity of these fabricated sensors against humidity has been observed. Furthermore, the improvement in response time can be correlated to an increase in effective diffusivity of water molecules and improved charge carrier mobility in the active sensing layer. It has been demonstrated that the TPPNi-ZnO semiconductor-based humidity sensor can operate effectively quasi-linearly in the bimodal (capacitive and resistive) mode for ambient relative humidity measurements with superior sensitivity and lowered recovery and response times when compared to a published set of humidity sensors. Furthermore, the associated intense and wide bandwidth spectral response of the TPPNi-ZnO nanocomposite makes it well suitable for its applications in light-harvesting heterostructures nanohybrids in future studies.

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Notes

The authors declare no competing financial interest.

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