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Mini-Review

Fabrication and Materials Integration of Flexible Humidity Sensors for Emerging Applications

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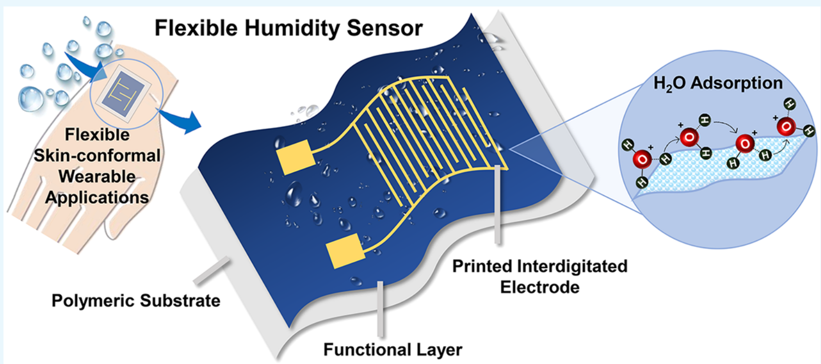

ABSTRACT: In the past decade, humidity measurements have ubiquitously gained consideration in the wide range of application paradigms such as industrial predictive maintenance, instrumentation, automation, agriculture, climate monitoring, healthcare, and semiconductor industries. Accurate humidity measurements and cost-effective fabrication processes for large-volume and high-performance sensors with flexible form factors are essential to meet the stringent performance requirements of the emerging application areas. To address this need, recent efforts focus on development of innovative sensing modalities, process technologies, and exploration and integration of new materials to enable low-cost, robust, and flexible humidity sensors with ultrahigh sensitivity and linearity, large dynamic range, low hysteresis, and fast response time. In this review paper, we present an overview of flexible humidity sensors based on distinct sensing mechanisms, employed processing techniques, and various functional sensing layers and substrate materials for specific applications. Furthermore, we present the critical device design parameters considered to be indicative of sensor performance such as relative humidity range, along with a discussion on some of the specific applications and use cases.

1. INTRODUCTION

Humidity, in general, is defined as the concentration of water vapor present in air. It plays a vital role in sustaining biological life on Earth. Alterations in humidity levels significantly influence the environmental conditions and life of living organisms. Therefore, it is absolutely necessary to constantly measure and monitor humidity levels under various environmental conditions. For instance, in the agriculture industry, the overall crop growth is strongly dependent on the moisture content of the soil. Additionally, processing, transportation, and storage of grains and cereal require optimum humidity levels to extend shelf life. On the other hand, in healthcare systems, humidity sensors are widely employed for respiratory equipment, incubators, sterilization processes, medicine production, and storage. Similarly, a wide range of humidity sensors are utilized for smart environmental control of buildings and infrastructures. Salient application domains of humidity sensors are illustrated in Figure 1.

In order to measure humidity levels with accuracy and precision in such a broad application spectrum, it is inevitable to enhance the characteristics of sensors in terms of sensitivity, linearity, hysteresis, repeatability, response time, dynamic range, and so forth to meet the specific requirements of each application. The need for humidity measurement under different circumstances leads to innovation on device structure design, material exploration, and advancement of fabrication technology. Moreover, miniaturization of humidity sensors together with the widespread demand necessitates new process technology solutions that offer ease of integration with the peripheral readout electronics and provide cost-effective batch-manufacturing capability.

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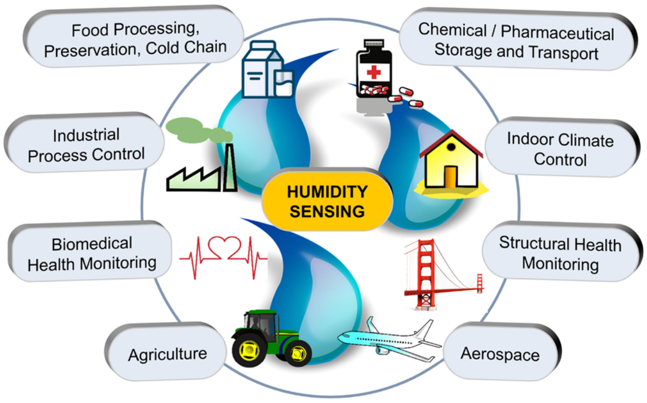

Figure 1. Various application paradigms of humidity sensors.

Flexibility of humidity sensors is a key aspect that has gained attention in recent works. Due to emerging application areas such as health monitoring and human−machine interfaces, the need for flexibility has grown even further.[1] To achieve durable and sensitive devices, it is crucial to choose and process appropriate sensing layers and substrates.

In terms of device architecture, the humidity sensor comprises a sensing/transduction layer over a substrate with electrodes placed for physical interfacing. Distinct types of humidity sensors are available, which are primarily differentiated by their sensing mechanisms including capacitive, resistive, and piezoelectric/surface acoustic wave and optical principles. Humidity measurement is generally quantified by two types of measurement units. Most often, it is expressed in terms of relative humidity (RH). Relative humidity is defined as the ratio of water vapor content present in air to the utmost

Table 1. Summary of Some Recently Reported Flexible Humidity Sensors

ref	sensing principle	flexible sensing material	RH range	*T* (°C)	sensitivity	response/recovery times (s)
6	capacitive	hydrophilic polytetrafluoroethylene	45−90%	35		
5	capacitive	cellulose acetate butyrate	10−70%		2.36 ± 0.08 fF/%RH	response: 24 ± 3 s recovery: 22 ± 4 s
7	capacitive	yarn (compositions: polyester (Coolmax, Pentas, and Cleancool) and polyimide fibers)	6−97%	25	82.4 pF/%RH (for Cleancool)	response: 3.5 s recovery: 4 s
24	capacitive	nanoscaled polypyrrole	30−90%			418 s
25	resistive	Ag/Fe_3O_4 NWs	11−95%	25	2.14 at 11%RH 64.67 at 95%RH	RH-dependent
9	resistive	functionalized multiwalled carbon nanotube/hydroxyethyl cellulose	20−80%	25	0.048/%RH	response: 20 s
11	resistive	PEDOT:PSS confined in 1D nanowire (core conductive PEDOT nanocrystal wrapped by nonconductive water-soluble PSS)	0−13%	37	5.46%	response: 0.63 s recovery: 2.05 s
10	resistive	polyvinyl alcohol/KOH polymer gel electrolyte (porous ionic membrane)	10.89−81.75%	25	10, 22, 30% at distances 0.5, 0.3, 0.1 cm	response: 0.4 s recovery: 2.6 s
4	resistive	poly(3,4-ethylenedioxythiophene)/reduced graphene oxide/Au nanoparticles	11−98%			response: 20 s recovery: 35 s
12	resistive	rGO/WS_2	0−91.5%	25	0.18/%RH	response: 31 s recovery: 95 s
26	resistive	CuO				response: 17.8 s recovery: 5.5 s
27	resistive	sulfonate polystyrene poly(3,4-ethylenedioxy- thiophene) (PEDOT) nanoparticles and graphene oxide (SPS:PEDOT NP/RGO)	0−98%	25	0.13−68.46%	response: 39 s recovery: 57 s
28	resistive/ capacitive	graphene oxide, poly(3,4-ethylenedioxy- thiophene) doped with poly(styrene sulfonate) anions (PEDOT:PSS) and $C_{15}H_{15}N_3O_2$ (methyl red)	0−100%	∼21	180 kΩ/%RH	response: 1 s recovery: 3.5 s
29	impedance	biopolymer kappa-carrageenan (KC) carbon nanotubes (CNTs)	20−90%	25		response: ∼200 s (20 to 80%RH)
30	impedance	polypyrrole (PPy)	20−97%	25		RH-dependent
15	piezoelectric	cadmium-doped zinc oxide nanowire nanogenerator (Cd−ZnO NW NG)	20−70%	25	85.7%	
17	piezoelectric	sodium niobate ($NaNbO_3$ NFs)	5−80%	24−80	2 mV/%RH	response: <12 s
16	SAW	graphene oxide microflakes (initially 50 μm)	10−85%	25	145.83 ppm/ %RH at 85%RH	response: 20 s (16−22) recovery: 5 s
22	optical	CdTe@Au/NaOH film	5−97%	25	254 au/%RH (5−to 50%RH) 910 au/%RH (50−97%RH)	response: 29 s recovery: 23 s

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(saturated) amount of vapor content that can be confined in air at specific temperature and pressure. Occasionally, humidity measurements are given as absolute humidity (AH), which measures the mass of vapor content in the air to the volume of air.

This paper primarily considers sensors based on RH and presents a brief review of ongoing research and development of flexible humidity sensors for a diverse range of applications. The flow is organized in such a way that section 2 explains the significance of material selection and presents flexible materials recently employed in sensors with different sensing principles; section 3 comprises various fabrication and processing techniques; some specific emerging application areas of humidity sensors are discussed in section 4, and finally, conclusion and outlook are presented in section 5.

2. FLEXIBLE HUMIDITY SENSORS

Flexibility is a direct result of the materials which are used mainly as sensing layers and substrates. The focus on this manner prioritizes obtaining and utilizing flexible materials which are not only promising in terms of humidity sensing but also lightweight, degradable, and low cost.

For sensing layers, materials such as graphene oxide (GO), carbon nanotubes and nanocoils and composites formed by polymers, ceramics, and semicoductors have been reported in the past works.[2] In such works, efforts are made to enhance the sensitivity of the materials through various methods. In Table 1, various flexible humidity sensors with different sensing layers are summarized.

For substrates, flexible materials such as polyimide (PI), polydimethylsiloxane (PDMS), polyester (PE), polyethylene naphthalate (PEN), and polyethylene terephthalate (PET) are the most commonly reported ones.[1,3] PI is a widely preferred material as a substrate due to its chemical stability, radiation resistance, electrical insulation, and temperature stability (190 to 540 °C). Similarly, PET is yet another widely employed flexible substrate,[4] owing to its adequate temperature resistance (120 °C), good adhesion properties, low manufacturing cost, and commercial availability.[5] Especially for conditions requiring tolerance to high temperature and stability of chemical properties, the PI substrate would be a better choice compared to PET.

Interest in these traditional organic materials has been lost because they suffer from issues such as degradability. To prevent such electronic debris, novel materials such as cellulose paper have also been reported to be functional, as both a sensing layer and a substrate.[1] Further investigation of recently utilized materials in sensors with different sensing principles are presented in section 2.1.

2.1. Capacitive Humidity Sensors and Material Integration.

Commonly studied and commercialized capacitive sensors rely primarily on changes in the dielectric permittivity of the sensing material placed between a pair of electrodes. In different studies, several approaches were taken to increase the nominal capacitance of the sensor.

For instance, the level of hydrophilicity of the dielectric film, hydrophilic polytetrafluoroethylene (H-PTFE), was enhanced by introduction of additional OH^- groups to the humidity-sensitive H-PTFE surface[6] (Figure 2a). This approach led to an increased capacitance 2×10^4 times that of its initial value with linear response.

A type of capacitive humidity sensor with a unique structure was reported by Ma *et al.*[7] Two copper wire electrodes were

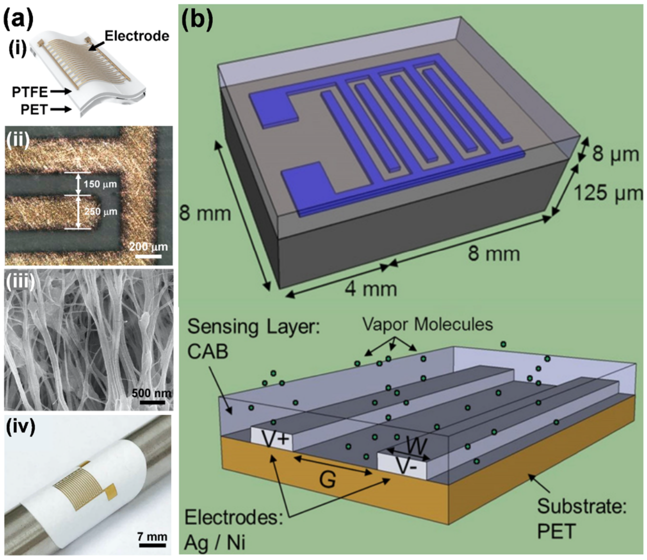

Figure 2. Capacitive humidity sensors. (a) Illustration and photograph of an H-PTFE humidity sensor, showing flexible properties where the H-PTFE and PET are used as the sensing layer and the substrate, respectively. Insets (ii) and (iii) show the optical microscope image of the electrodes and field-emission scanning electron microscopy image of the sensing membranes. Adapted with a CC BY license from ref 6. Copyright 2018 MDPI. (b) Sensing mechanism of a capacitive humidity sensor with cellulose acetate butyrate as the sensing layer and Ag/Ni as the electrodes. Sensing layer swells due to humidity and its dielectric constant changes. Adapted with permission from ref 5. Copyright 2012 Elsevier.

wrapped by yarns with different cross-sectional areas, initially around the first wire and then around both wires, resulting in a biaxial-sheathed form. Yarns with more surface channels showed better performance since more water molecules could be transported through the channels. Hysteresis was low during the measurements.

Some approaches were also developed to improve hydrophilicity of the sensing layer, including treatment of the hydrophilic polytetrafluoroethylene (H-PTFE) with sodium hydroxide (NaOH) to further improve the hydrophilicity of the H-PTFE surface by introducing additional hydroxyl (OH) groups, thereby achieving enhanced sensitivity.[6]

In another work, cellulose acetate butyrate (CAB) was used as the sensing layer on the PET substrate (Figure 2b).[5]

2.2. Resistive Humidity Sensors and Material Integration.

Resistive sensing is another most widely employed mechanism, and it is attributed to ionic conductivity that takes place in the sensing layer. Resistance response to increasing RH may have a positive or negative trend, depending on the sensing layer and accordingly the mechanism employed.

One resistive sensing example is the study reported by Mondal *et al.*,[8] where anodic aluminum oxide (AAO)-assisted molybdenum disulfide MoS_2 (referred to as AMHS) was utilized to construct a humidity sensor which achieved a sensitivity value of 668 (unitless), far exceeding the sensitivity level of designs based on bare MoS_2 film-based sensors (Figure 3a).

In a different work, a resistive sensor with functionalized multiwalled carbon nanotube (FMWCNT)/hydroxyethyl cellulose (HEC) as the sensing layer (Figure 3b) was reported.[9] In the MWCNT network, conduction is led by holes. Due to the electric potential difference between the

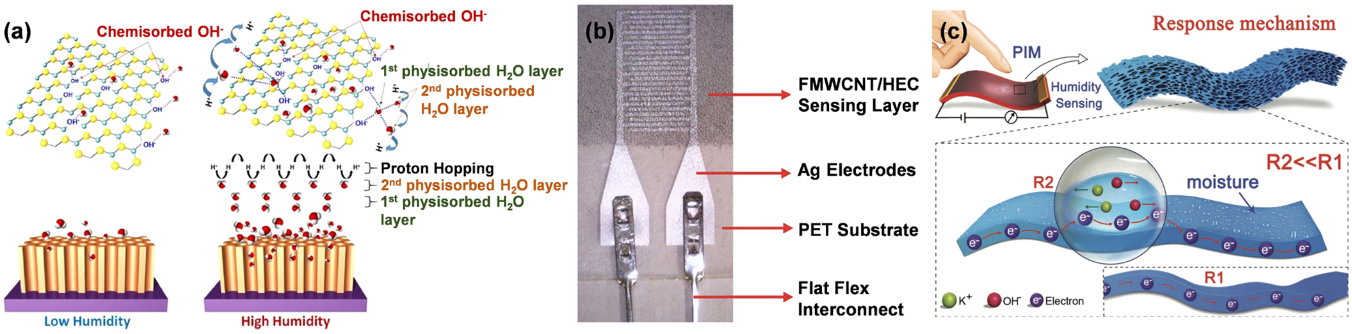

Figure 3. Resistive humidity sensors. (a) Proton hopping: H^+ ions bonding with H_2O molecules to form hydronium ions (H_3O^+) which then release H^+ to their neighbor H_2O molecules, causing a continuous hopping among consecutive H_2O molecules. Adapted from ref 8. Copyright 2020 American Chemical Society. (b) Photograph of a printed FMWCNT/HEC humidity sensor. Adapted with a CC BY license from ref 9. Copyright 2019 The Royal Society of Chemistry. (c) Sensing mechanism of a PIM-based sensor. K^+ and OH^- ions are released from the PVA to the moisture layer, increasing the amount of moving electrons and decreasing the resistance. Adapted with a CC BY license from ref 10. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

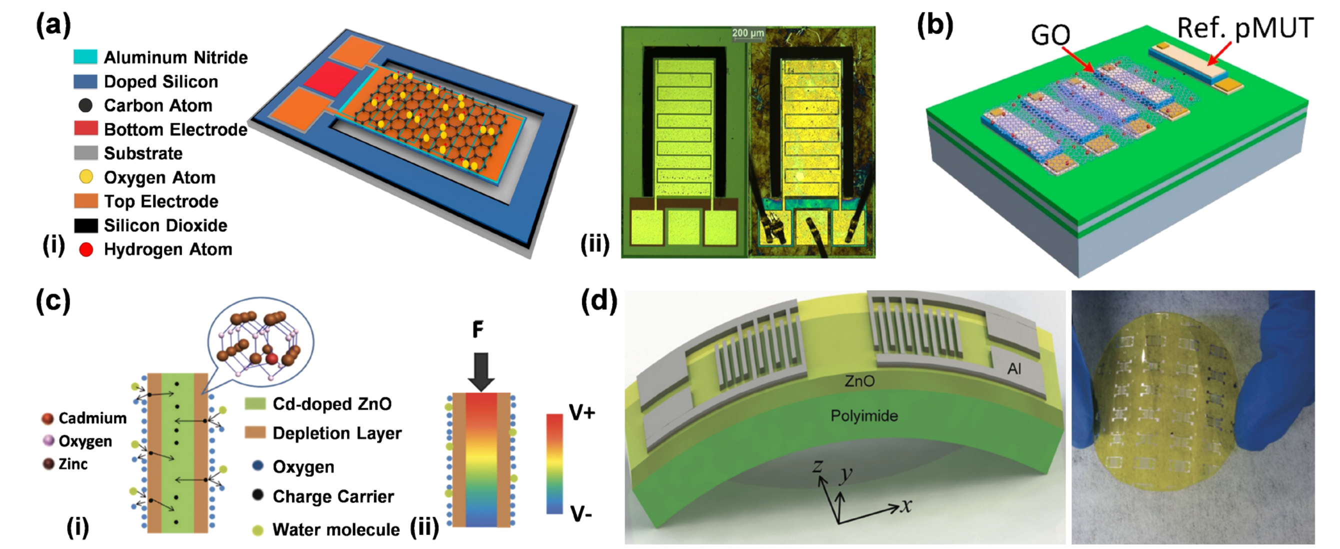

Figure 4. (a) Resonant cantilever-type piezoelectric humidity sensor with GO film as the sensing layer: (i) design and materials of the cantilever, (ii) optical micrograph of the sensor with and without the GO coating. Adapted with permission from ref 13. Copyright 2019 IEEE. (b) Piezoelectric micromachined ultrasonic transducer (pMUT) with GO as the sensing layer. Adapted with a CC BY license from ref 14. Copyright 2018 MDPI. (c) Sensing mechanism of a piezoelectric humidity sensor: (i) Electron vacancies in depletion layer are replaced by water molecules upon adsorption, electrons are released and depletion layer shrinks. An increase in free electrons means a decrease in voltage output. (ii) When force is applied, free electrons are dislocated and a voltage spectrum is observed due to the screening of piezoelectric polarization charges. Adapted from ref with permission from ref 15. Copyright 2015 Owner Societies. (d) Illustration and photograph of a SAW humidity sensor based on Al electrodes and piezoelectric ZnO thin films. Adapted with a CC BY license from ref 16. Copyright 2015 The Royal Society of Chemistry.

water molecules and the MWCNTs, electrons from the water molecules that are being adsorbed start to join the MWCNT network, filling these holes. As the number of holes decreases, resistivity increases. Additionally, because of adsorption, HEC swells, which results in a widened contact and increased resistance. The resistance changes by 290%. Similarly, in another work, one-dimensional nanoconfined PEDOT:PSS was utilized as the sensing material.[11] PSS acts as a shell to PEDOT. By water adsorption, PSS swelling is observed and the spacing between PEDOTs increases, leading to an increase in resistivity. This sensor remains operational and maintains performance while experiencing bending up to 1000 times.

In the work reported by Li *et al.*,[10] potassium hydroxide (KOH) concentration was altered to impact the conductivity of the porous ionic layer (PIM) made up of poly(vinyl alcohol) (PVA)/KOH gel electrolyte (Figure 3c). Since the solubility of KOH is better in water than it is in PVA, some potassium and hydroxide ions can migrate from PVA into adsorbed water, effectively increasing the amount of transferred electrons and lowering the resistance. As such, conductivity of the porous-sensing membrane was observed to increase by a factor of 70 while achieving a temperature invariant operation.

Another humidity sensor with reduced graphene oxide (rGO) as the sensing layer was reported, and two alternatives (rGO and rGO enhanced with WS_2 nanoparticles) were compared. The rGo/WS_2 sensor was found to be more sensitive than the rGO sensor.[12]

2.3. Piezoelectric Humidity Sensors and Material Integration.

Humidity sensors comprising the piezoelectric effect are proposed as a reliable indicator for humidity levels with an added benefit of an energy-harvesting mechanism to enable self-powered devices.

In the work published by Gu *et al.*,[17] $NaNbO_3$ nanofibers were proposed as enablers for flexible humidity sensors, along

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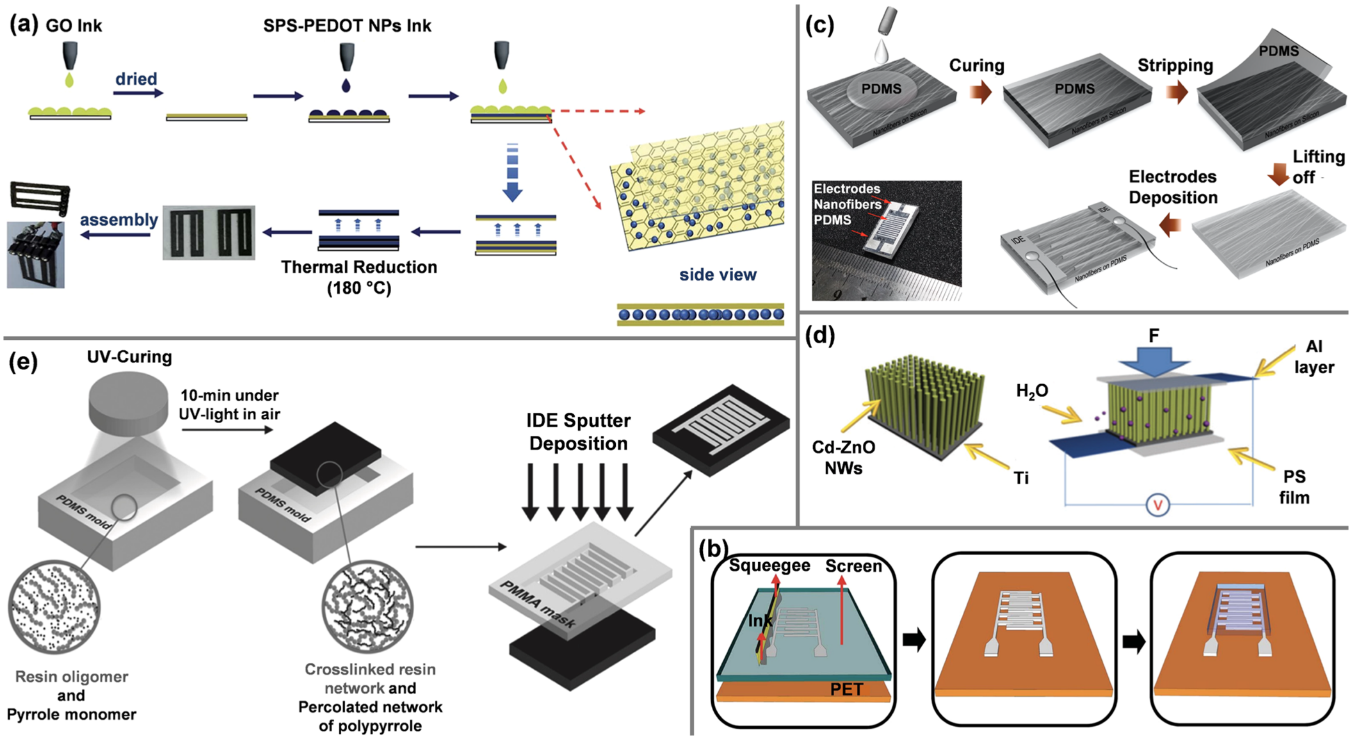

Figure 5. (a) Inkjet-printed GO and SPS-PEDOT nanoparticles, thermal annealing process. Adapted with permission from ref 27. Copyright 2016 The Royal Society of Chemistry. (b) Screen-printed Ag electrodes and gravure printed FMWCNT/HEC-sensing layer. Adapted with a CC BY license from ref 9. Copyright 2019 The Royal Society of Chemistry. (c) Synthesis of $NaNbO_3$ nanofibers by far-field electrospinning, spin-coating of PDMS onto nanofibers, lift-off to transfer nanofibers onto PDMS, and electrode deposition by sputtering through a shadow mask. Adapted with a CC BY license from ref 17. Copyright 2016 MDPI. (d) Growth of Cd−ZnO nanowires by wet chemical method, final device structure. Adapted with permission from ref 15. Copyright 2015 Owner Societies. (e) Polymer network formation by UV-curing followed by interdigitated electrode deposition using DC sputtering with acrylic (PMMA) shadow mask. Adapted with permission from ref 30. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

with a provision of piezoelectric energy harvesting, which is facilitated by flow of electrons to an external circuit and generation of a piezoelectric potential under bending stress.

A resonant cantilever relying on the high mode of the resonator harnessed GO and aluminum nitride (AlN) as the sensing and piezoelectric layers, respectively (Figure 4a).[13] Frequency shifts were tracked at normal and interdigital transducer (IDT) excitations, which displayed small hysteresis.

Similarly, a piezoelectric micromachined ultrasonic transducer (pMUT)-based sensor topology was demonstrated to observe frequency shifts with humidity, where GO was deposited as the sensing layer (Figure 4b). The presence of humidity leads to interlayer expansion between GO layers and results in the formation of an internal stress on the pMUT layer. Accordingly, the PMUT resonance frequency shifts with humidity, and sensitivity values up to 719 Hz/%RH can be achieved.[14]

Alternatively, electron detection can also play a vital role in humidity sensing. A cadmium-doped ZnO nanowire nanogenerator was reported as a piezoelectric humidity sensor based on the electron detection principal illustrated in Figure 4c.[15] By cadmium (Cd) doping many oxygen vacancies are formed on the surface of nanowires, enhancing humidity-sensing performance. At RH values of 27, 37, and 65% RH, the induced voltage measurements were approximately 0.217, 0.173, and 0.050 V, respectively.

Humidity sensors employing surface acoustic wave (SAW) devices offer additional advantages such as less cost, low power, and ease of fabrication. Typically, SAW devices are fabricated on silicon and polyimide substrates; some works on PEN flexible substrates have also been demonstrated, using crystals of $LiNbO_3$ or $LiTaO_3$ as the piezoelectric material.[18] Another work proposes high-performance lamb-wave SAW flexible humidity sensor employing GO as the sensing layer fabricated on a piezoelectric ZnO film deposited on flexible polyimide substrates (Figure 4d).[16] Similarly, flexible and transparent SAW sensors using a ZnO piezoelectric layer on PI/PET substrates were reported, where addition of a GO-sensing layer has significantly improved the humidity sensitivity.[19]

2.4. Optical Humidity Sensors and Material Integration. Although humidity sensors based on optical fibers are not typically printed on plastic substrates, due to the flexible nature of especially plastic optical fibers, it is still worthwhile to treat them as "flexible humidity sensors" given their widespread use and some major advantages. Fiber-optic humidity sensors are relatively noise immune and can transmit data over long distances owing to the low attenuation of fibers, rapid response potentially enabling real-time monitoring, high sensitivity, and the ability to be deployed in harsh environments especially for industrial process monitoring in contrast to conventional humidity sensors.[20]

Optical sensors based on absorbance also include those based on the adsorption of water molecules on the sensing film. For instance, an optical humidity sensor coating a xerogel film at the tip of a multimode optical fiber as a sensing layer, producing two interfaces including fiber xerogel and xerogel vapor, was reported.[21]

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It has been shown that the reflectance of the film is decreased by increasing the concentration of water vapor in the chamber. Enhancing the overall sensitivity of the sensing film and analyzing the effective parameters to improve sensing performance is indeed a matter of interest in the sensing mechanism. For instance, Chen *et al.*[22] shows that adding Au nanoparticles on the sensing film enhances the overall performance.

An evanescent wave sensor was proposed including a sensing film of cobalt dispersed in polyaniline nanocomposites which was dip-coated onto a section of the fiber where the cladding was removed.[23] This allowed a portion of the evanescent wave to be absorbed by the sensing film where the absorbed optical power changed with environmental humidity level.

3. PROCESSING TECHNIQUES

While some unconventional processing techniques have been reported, printing processes such as inkjet, gravure, and screen printing are the most widely used approaches in fabricating flexible humidity sensors.

3.1. Inkjet Printing. Inkjet printing is a versatile technique to fabricate flexible humidity sensors as it allows maskless patterning and offers deposition of a variety of ink chemistries. One example is a capacitive-based humidity sensor fabricated on PET susbtrates by inkjet printing of CAB as the sensing layer and silver nanoparticle based inks to form the interdigitated electrode structure.[5]

Similarly, the inkjet-printing method was employed to fabricate a sensor with an RH range of 0 to 100% using three IDT electrodes connected in series with combination of PEDOT (poly3,4-ethylenedioxythiophene)-doped poly(styrene sulfonate) anions (PEDOT:PSS), $C_{15}H_{15}N_3O_2$ (methyl red), and GO.[28]

Last but not least, the inkjet-printing technique was utilized to develop a humidity sensor based on nanoparticles on the PET substrate with RH in the 11−98% range.[4] Specifically, PEDOT, rGO, and reduction of gold nanoparticles (NPs) modified with polyethylenimine (PEI) were utilized to form a PEDOT:rGO-PEI/Au nanoparticle ink which was then deposited using inkjet printing, chemical vapor deposition, drop-coating, and casting methods on a substrate surface to obtain a PET-based sensor.

Lastly, a layer-by-layer inkjet-printing method was employed to overcome the difficulties in PEDOT printing during its passage through the nozzle of a standard printer.[27] In this work, the prepared sulfonate polystyrene:PEDOT nanoparticles (SPS:PEDOT NPs) and rGO were used to form a composite film on the PET substrate after thermal annealing (Figure 5a).

3.2. Gravure and Screen Printing. The compatibility with roll-to-roll processing renders gravure and screen-printing techniques favorable toward mass fabrication of low-cost, flexible humidity sensors. So far, several studies demonstrated the use of gravure and screen-printing approaches where different substrate-sensing layer combinations were studied.

An alternative approach which merges gravure and screen-printing approaches was employed to fabricate a composite-based humidity sensor with silver electrodes and functionalized multiwalled carbon nanotubes as the sensing layer (Figure 5b).[9] Likewise, fabrication of an ammonia sensor, which was also tested as a humidity sensor, included gravure-printing and screen-printing techniques. A polyaniline-sensing layer was gravure-printed onto the PET substrate followed by screen printing of carbon-based electrodes onto polyaniline to complete the fabrication. Reproducibility of these methods was demonstrated through fabrication of a batch of sensors and testing under similar conditions.[31]

Cleanroom processes, albeit generally being costly, were also used to fabricate humidity sensors. One approach which could potentially be scaled for roll-to-roll production, employed a nanoimprint technique to create nanochannels as templates to guide formation of parallel PEDOT:PSS nanowire arrays directly on the PET substrate upon evaporation of an aqueous solution of PEDOT:PSS.[11]

3.3. Unconventional Methods. Apart from inkjet, gravure, and screen printing, processing techniques which are not typically standard to roll-to-roll fabrication have also been used to demonstrate humidity sensors.

For instance, composite-based sensors were realized by using flexible kappa-carrageenan (KC) and carbon nanotubes (both single-walled and multiwalled) by an evaporative casting method.[29] Similarly, piezoelectric sodium niobate ($NaNbO_3$) nanofiber-based humidity sensors were reported where nanofibers were prepared by far-field electrospinning on silicon substrates and then transferred to PDMS elastomers.[17] The transfer procedure involved a three-step approach including spin-coating PDMS, curing, and lifting off the PDMS from the substrate. Upon transferring of nanofibers, interdigitated electrodes were formed by sputtering on a shadow mask to complete the device fabrication (Figure 5c).

In another work, PVA solution and prepared cold aqueous solution of KOH forming a PVA/KOH polymer gel electrolyte was used to fabricate a flexible PIM sensor using solution casting process.[10]

More along the solution-phase-based facile approaches include studies that involve wet-chemical synthesis of humidity-sensitive layers followed by packaging techniques as simple as taping or gluing. For example, a cadmium-doped ZnO piezoelectric nanowire (NW)-based flexible humidity sensor was realized by chemical synthesis of Cd−ZnO NWs, which were then coated on titanium foil by immersing the foil into NW solution. The device fabrication was completed by attaching aluminum foil with the help of silver paste (Figure 5d).[15]

Polymerization-based techniques were also employed to develop flexible humidity sensors. One example is a work on polymerization-induced adsorption to form nanoscaled polypyrrole (PPy) layer on cellulose surfaces to form capacitive-type flexible humidity sensors made of cellulose−polypyrrole nanocomposites.[24] Alternatively, photochemical polymerization of PPy (Figure 5e) was reported, wherein simultaneous UV-curing of an insulating network (acrylic or epoxy) was performed and a one-step fabrication method was demonstrated.[30]

Spray coating and its variants are yet other approaches to effectively realize moisture-sensitive, stable coatings on polymeric substrates. For example, a kinetic spraying method was used to implement a semitransparent flexible humidity sensor based on cupric oxide (CuO) as the sensing layer, where copper particles were deposited by a nanoparticle deposition system and later oxidized by annealing in ambient air to achieve CuO layer with good adhesion to polyimide substrate.[26]

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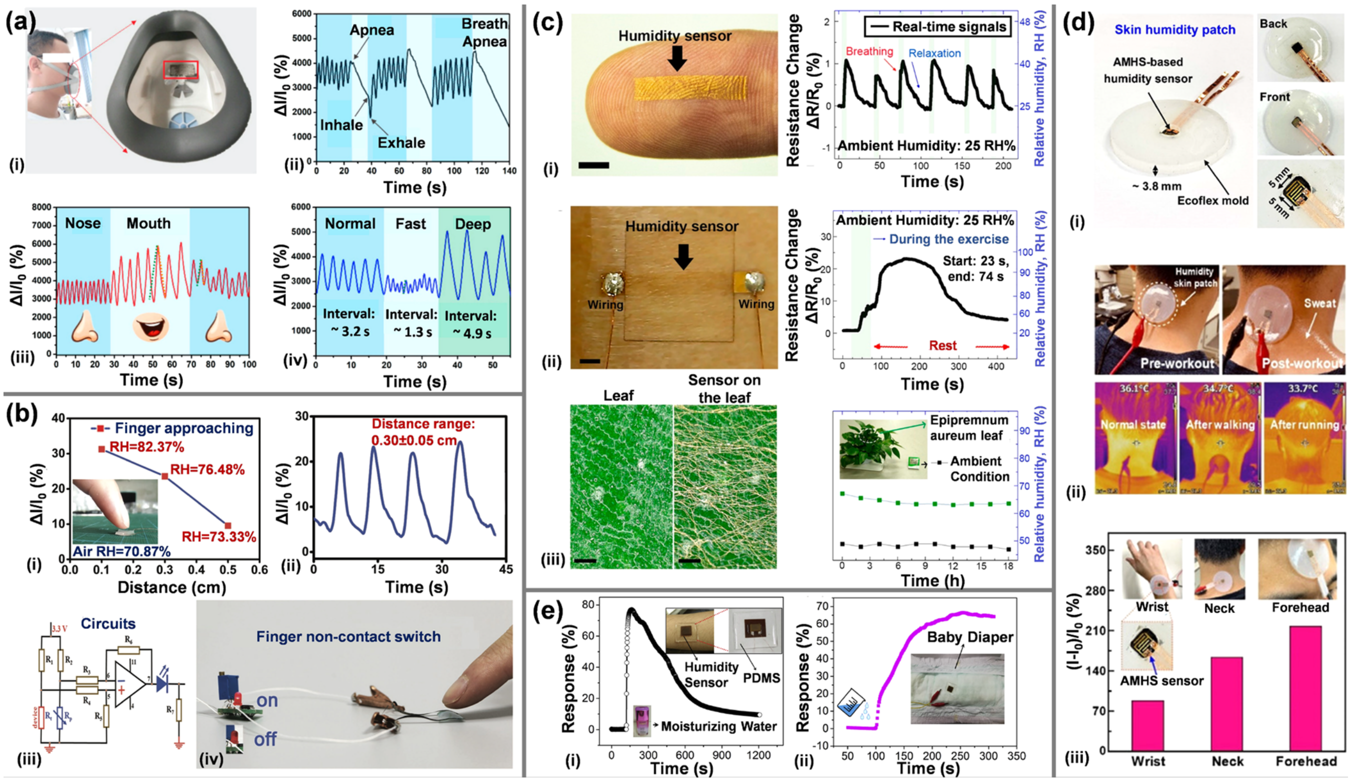

Figure 6. (a) Ag@Fe_3O_4-MS sensor: (i) sensor placed inside a respirator, (ii) breathing patterns that represent inhaling, exhaling, and apnea periods, (iii) nose and mouth breathing, (iv) detection of normal, fast, and deep respiration. Adapted with a CC BY license from ref 25. Copyright 2019 MDPI. (b) Porous ionic membrane based humidity sensor: (i) sensor response at different distances with approaching finger, (ii) repeatability through four cycles, (iii) circuit schematic, and (iv) demonstration of a noncontact switch. Adapted with a CC BY license from ref 10. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Nanomesh humidity sensor tested on (i) a human finger, (ii) skin on the backside of a human body, and (iii) a plant leaf, where response due to changes in human breath, sweat, and ambient humidity conditions was monitored. Adapted from ref 32. Copyright 2019 American Chemical Society. (d) AAO-assisted MoS_2 (AMHS)-based humidity patch: (i) photograph of the sensor patch, (ii) pre- and post-workout photographs of the patch attached to the neck and IR images at different temperatures during normal, after walking, and after running states, (iii) measurements on relative current obtained when the patch is located on wrist, neck, and forehead. Adapted from ref 8. Copyright 2019 American Chemical Society. (e) Response of MWCNTs/PLL sensor to humidity changes on (i) skin and (ii) baby diaper. Adapted with permission from ref 33. Copyright 2019 Elsevier.

4. EMERGING APPLICATIONS

Numerous humidity sensor applications are presented in the literature, predominantly for medical purposes. Many reported works have demonstrated prototypes of applications which are promising in terms of the sensitivity and applicability.

Particularly in respiration tracking, humidity sensors with fast response are quite useful. During respiration, warm and humid air is exhaled, whereas dry air is inhaled, and this pattern is analyzed to detect abnormalities in breathing proficiently. A flexible humidity sensor was attached to a subject's finger and placed in front of their nose within a 3 cm range. A wireless transmission system was formed, and a Bluetooth chip transmitted the signals to a mobile phone for tracking respiration. Deep, rapid, and normal respiration as well as the apnea periods in the sleep cycle were reported to be distinguished successfully.[11]

Similarly, a yarn-shaped sensor was stitched inside a mask.[7] An LC wireless system was formed for signal transmission in order to develop a smart mask. Results of this work have proven consistency with a commercially available sensor. With an exceptional approach, sensors by Zhang *et al.*[25] were designed to be easily cut into pieces to broaden usage opportunities. In the first demonstration, the Ag@Fe_3O_4-MS sensor was placed inside a respirator with the aim of detecting apnea and respiration patterns (Figure 6a). Aside from these, breathing from the nose and mouth were also distinguished properly. As a second application, some pieces were darned onto a mask and sleeve. By this application, hydration status of a person before and after drinking water as well as the humidity level of skin was tracked successfully.

Polyelectrolyte humidity sensors offering very fast response times were utilized for monitoring and detection of specific respiration patterns or breathing rates including normal, slow, fast, deep, random, and paused breathing. The developed humidity sensors were also tested in touchless sensing applications where the moisture and sweat in the fingertip causes local fluctuations in the relative humidity level of the ambient air above the sensor surface. In a PIM-based sensor, this principle was used to track RH changes that rise from an approaching finger, along with an alternative use case scenario in wellness and skin-care applications where water content on facial skin was monitored at different conditions including usage of cosmetic products[10] (Figure 6b). The results revealed that a linear trend exists between the sensitivity and the water content on face and proved to be consistent with measurements obtained with commercial sensors.

Besides respiration tracking, sweat tracking have also gained attention over the years. A breathable humidity sensor was experimented on a finger, on skin and on a plant leaf (Figure

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6c).[32] The unique nanomesh structure provided enhanced breathability, where sensor performance was verified by testing with human breath, sweat during exercise, as well as tracking relative humidity levels on the surface of a plant leaf. As another humidity sensor application for tracking of the sweat rate, an anodic Al_2O_3-assisted MoS_2 honeycomb structure based humidity sensor was proposed (Figure 6d).[8] Response data were collected using the patch sensor before exercise, after walking, and after running. In addition, the patch was tested on the wrist, neck, and forehead, and a comparison of relative current variations was reported.

Another useful application is to track the wetness of baby diapers. A MWCNTs/poly-L-lysine (PLL) composite film based sensor was fabricated and tested for this purpose. When compared to pure MWCNT sensors, the fabricated composite film responded to RH changes better due to the hydrophilic nature of PLL. Skin moisture and also wetness of baby diapers were detected correctly and the response of the sensor is illustrated in Figure 6e.[33]

Not least of all, Park *et al.*[6] demonstrated a real-time monitoring setup where a humidity sensor was placed on a curved surface. The system was located above a beaker with water and then removed, such that changes in environmental humidity levels were tracked through continuous signal transmission to a mobile phone.

5. CONCLUSION AND OUTLOOK

In this review paper, a variety of materials, fabrication techniques, and sensing mechanisms which have been exploited for flexible relative humidity sensors have been surveyed to demonstrate the state-of-the-art and provide a critical review on their performance along with a discussion on possible application areas. Based on recent development trends we envision that, flexible humidity sensors will keep gaining attention as they prove to be useful for numerous applications in which the sensor element either has to be bent, stretched, or flexed as in wearable applications or need to conform to preconfigured surfaces, which at the same time may happen to reside in extreme environments. Fortunately, typical process technologies used in fabrication of flexible humidity sensors harness the advantages of roll-to-roll manufacturing, which cuts from production costs and time and plays in favor of the development trends. New processing techniques which may enable mass production and further enhance mechanical endurance should also be explored. While the market is currently dominated by humidity sensors that rely primarily on capacitive and resistive sensing principles, developments in optical and piezoelectric sensors also show promise owing to their unique benefits in noise immunity and self-powered operation, respectively. Strong focus should be placed on novel materials to advance the sensors in terms of flexibility, degradability and durability. With further developments in humidity-sensitive functional inks, substrate materials, and process technologies, low-cost and ubiquitous flexible humidity sensors with superior sensitivity and range will be possible which are also expected to lead into new, emerging IoT and IoHT applications.

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Notes

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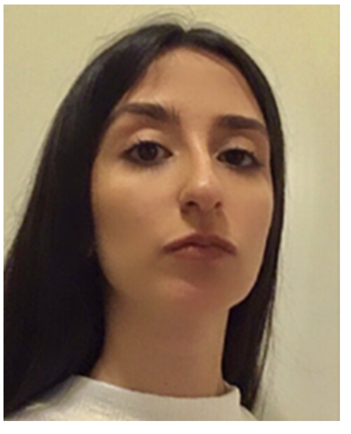

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