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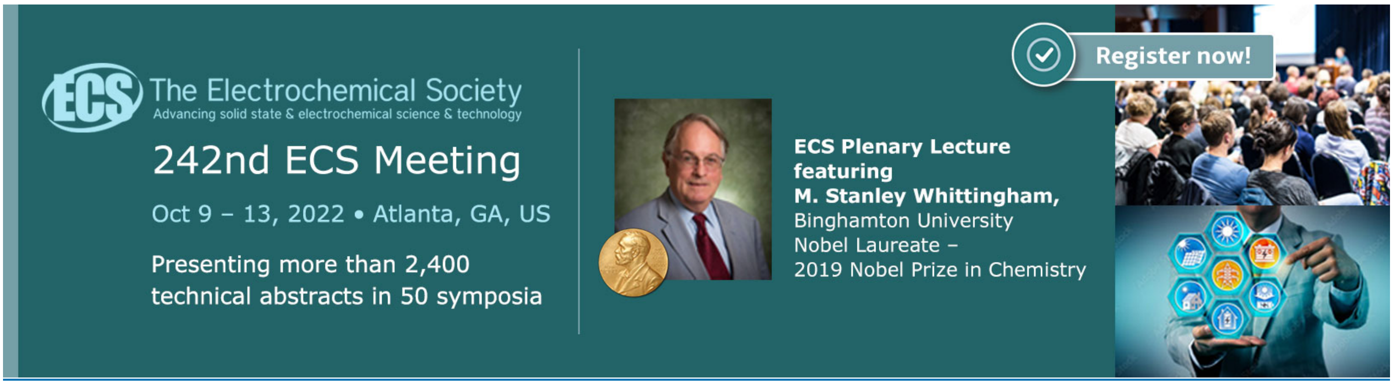

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Perspective—Conducting Polymer Hybrids as Diagnostic Chemosensors

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Polyaniline is a conducting polymer in which both redox and protonating/ deprotonating conduction mechanisms are activated in the presence of gaseous compounds, making it a gas sensor. Resistive chemosensors based on PANI, in particular, have been well studied for their gas sensing properties and are considered important sensing materials for a wide range of applications as they operate at room temperature. There is, however, a novel class of polyaniline hybrids with cellulose acetate that may be suitable for detecting biomarkers emitted from the skin and in measuring the pH of breath condensate for diseases and thus, worth studying them further.

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Polymers are repeating units of carbon chains with immobile electrons bound by covalent bonds formed between carbon and other atoms making them insulating in nature. A class of polymers termed "electroactive" consists of conjugated chains, whereas the system is comprised of atoms with alternating single and double bonds with the latter consisting of p orbitals. The structure is said to consist of delocalized bonds (the superposition of 2p atomic orbitals between atoms in a covalent double bond[1]) which can be manipulated by chemical or electrochemical means to alter the density of charge (i.e. electrons or protons) within the conjugated species.

Manipulation of these chains by reduction/oxidation mechanisms (via changes in number of electrons) and in the case of polyaniline, protonation/deprotonation (change in number of protons while the number of electrons remain unchanged) has led to the development of intrinsically conducting polymers—ICPs. These are "electroactive" polymers that possess electronic and magnetic properties while retaining their structural characteristics.[2] ICPs are a class of polymers that can be made conducting without the use of conductive additives. Examples of conducting polymers studied for sensing applications are polypyyrole, polythiophene, poly (3,4-ethylenedioxythiophene), poly(phenyl vinlene), and polyaniline. Conducting polymers such as polypyrrole and polyaniline have been widely researched for gas detection. For example, chemoresistors based on polyaniline has shown higher sensitivities (low limit: 0.5 ppm for NO_2)[3,4] as compared to polypyrrole based chemoresistors (low limit: 20 ppm for NO_2).[5] Current advancements in polyaniline based environmental gas sensors are outlined in various reviews, e.g..[6] This work is our Perspective on the need of hybrid PANI-CA materials for use in detecting biomarkers emitted from the skin and in measuring the pH of breath condensate for diseases.

Current Status-Polyaniline for Resistive Chemosensors

The monomer aniline was first reported in 1862 by Letheby[7] and was synthesized to form different oxidation states by[8–11] in the early 20th century. It was later sought in the late 70's by[12] that the polymer polyaniline can be made conducting via chemical or electrochemical doping mechanisms. The traditional routes for producing polyaniline are chemical oxidative polymerization and electrochemical oxidative polymerization (which occurs in an electrochemical cell—two or three electrode). Generally, the synthesis of polyaniline can be expressed as follows: the aniline monomer is first dissolved in an acidic solution (i.e. dopant solution such as HCl) (in this case a proton is transferred from HCl to the monomer). An oxidant (such as ammonium peroxydisulphate) transforms it to the anilium cation, which then reacts with other units through hydrogen bonding to form diamine chains which react with other chains to form the extended conjugated network. This process produces the highest oxidation form (pernigraniline). A reductant (i.e. NaOH) can then be employed to produce the other polymer forms.

The base structure of polyaniline consists of a reduced unit or benzenoid attached to an amine (−NH−), and an oxidized unit or quinoid attached to an imine (−N=). The amines and imines are the nitrogenous centers of polyaniline which may react with dopant agents and/or analyte and the ratio of amines to imines dictates the oxidation state.

Polyaniline exists in several oxidized forms. The most studied and widely accepted are the leucoemeraldine which is the fully reduced form, $y = 1$, the emeraldine form which is half oxidized, half reduced, $y = 0.5$, and the pernigraniline form which is the fully oxidized form, $y = 0$. Transformations between oxidation states are reversible and controlled using reducing or oxidizing mechanisms. During oxidation of leucoemeraldine base the oxidant removes an unbound electron from the amine nitrogen center, a proton is liberated, and the lone unbound electron resonates to a neutral position, forming an imine.

Leucoemeraldine can be oxidized to emeraldine and then pernigraniline. From pernigraniline, leucoemeraldine can again be obtained by reducing pernigraniline to emeraldine and finally back to leucoemeraldine with an alkaline solution (i.e. NaOH). The emeraldine base is deemed the most stable form of polyaniline that is because further oxidation of the pernigraniline state results in degradation of the polymer back to emeraldine and leucoemeraldine can be easily oxidized in air. Thus, the most widely used and widely studied form of polyaniline is the emeraldine form.

Doping mechanisms.—All three states can exist in the base and salt form. In the former the polymer is insulating and upon doping can be transformed into a conducting salt. The highest conducting form is the emeraldine salt (ES-PANI). The two most common methods used to produce ES-PANI are oxidative doping of leucoemeraldine base (LEB-PANI) and protonic acid doping, of emeraldine base (EB-PANI) (see Fig. 1). Both methods result in the creation of reactive sites delocalized along the polymer backbone through which charge transport can occur.

Oxidative or p doping is a two-step process which starts with oxidation (an example of an oxidant is H_2O_2) of LEB-PANI yielding the partial removal of electrons from the polymer chain and doping with an acid (i.e. camphorsulfonic acid or HCl) to incorporate

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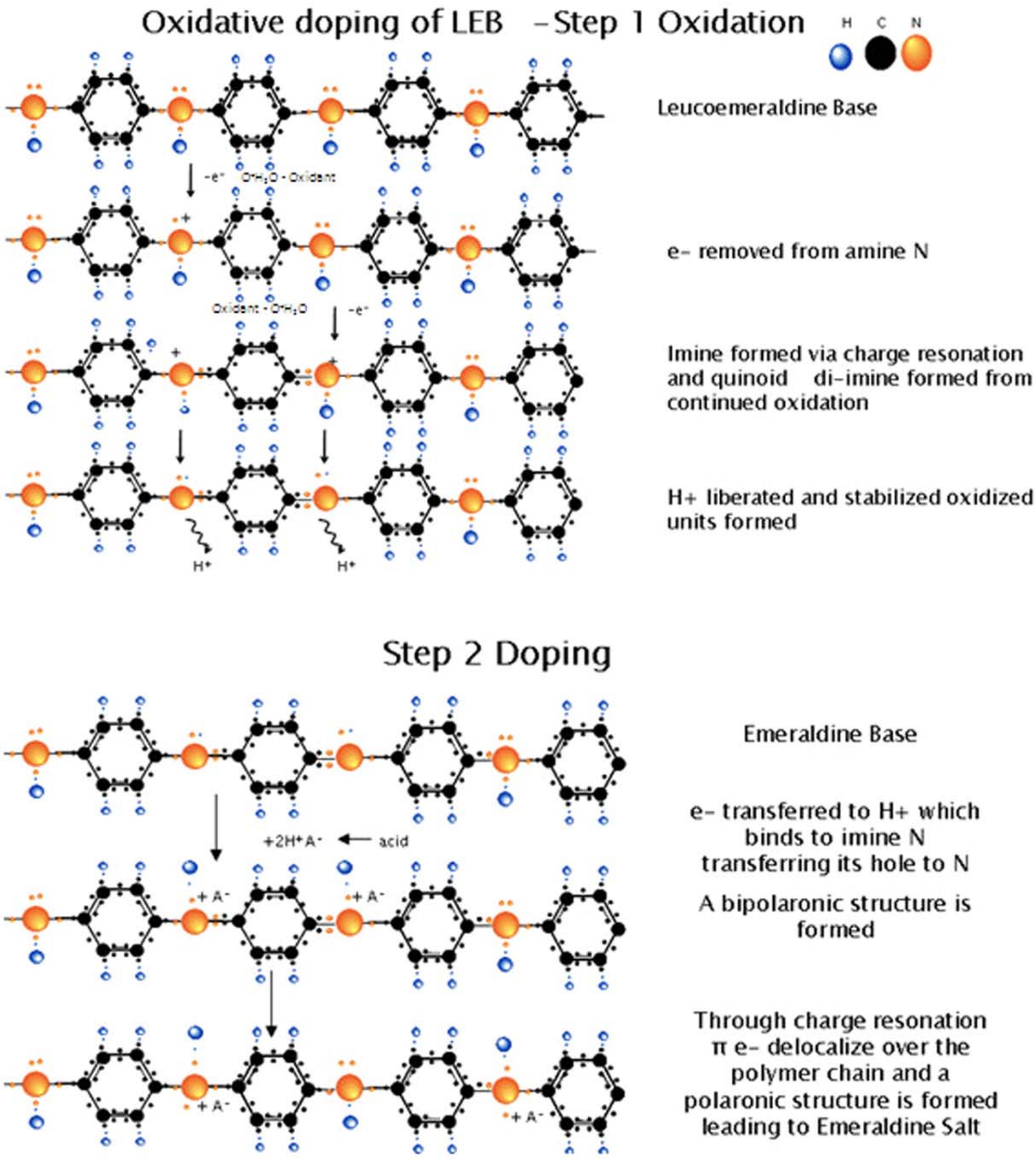

Figure 1. Oxidative doping mechanism from LEB-PANI to ES-PANI. The steps are interchangeable and either one can occur 1st during the chemical/electrochemical reaction.

molecular impurities at the same sites through the addition of holes and anions (in the case of HCl, H^+ is the hole or positive charge and Cl^- is the anion).[13] During doping, the polymer becomes positively charged and anions provide charge neutrality. In theory, pernigraniline base (PB-PANI) can also undergo reduction or n doping to produce ES-PANI, where cations are inserted at the sites where electrons are added imparting a negative charge on the polymer chain.

Reductive or n doping however is not commonly employed for preparing ES-PANI. The impurities added to the polymer can induce localized distortions (associated with the charge on the site) in the conformational structure (i.e. ring torsion). These distortions are coupled with defects called polarons (primary charge carriers formed during doping and oxidation; a positive polaron is formed when a hole is coupled with an anion—typically resembles the form of an amine) and bipolarons (charge carriers formed when secondary charges are removed from the electronic structure; not energetically stable and is typically centered around a quinoid di-imine group).

Protonic acid doping of EB-PANI can yield a positively charged polymer from the addition of protons (coupled with an anion) at imine sites along the polymer chain while the number of electrons in the system remains unchanged. The protons and anions added to the system also induce distortions coupled with polarons and bipolarons along the polymer chain. The emeraldine salt form produced through this mechanism consists of $-N^{+}H-$ units throughout the matrix. $H^{+}Cl-$ is also a common protonic acid employed for this process. Currently protonic acid doping is the more popular doping mechanism employed for producing ES-PANI. The defect sites act as charge carriers and tunneling bridges for ions. Moreover, the dopant anions (cations for n doped materials) can react with analyte molecules with higher sensitivity and selectivity depending on the anion and target analyte.[14] These mechanisms can impart electrical conductivities in polyaniline up to 10^{-1} S cm^{-1}.[13]

Conduction Pathways in Polyaniline

Electronic conduction in polyaniline is a function of interchain, interdomain, and intrachain charge transport where

$$\sigma = nq\mu = \mathrm{f(interdomain;\ interchain;\ intrachain)}$$

and n is the number of carriers, q is the charge on the electrons and μ is the mobility.

Intrachain electrical conductivity has dependence on conjugation length and number of defects in the system. Interchain and interdomain electrical conductivity has dependence on degree of crystallinity (the increase in crystallinity allows for an increase in charge hopping sites).

Researchers have developed models to explain the electron-phonon interactions in polyaniline as ions move through its matrix. For low doped polyaniline (where few sites along the chain have been doped—not highly conducting) the widely accepted variable range hopping mechanism[15,16] has been employed to prove that at low temperatures, in a disordered system (such as a conducting polymer) the charge transport mechanism is governed by hopping and/or tunneling mechanisms along doped/conducting sites. As the doping and oxidation level increases, molecular chain arrangements resulting in interchain coupling and intrachain order[17–19] can cause phase segregation of the polymer into crystalline conducting regions and amorphous insulating regions.[20] It has been shown[20] that charge transport for these materials depends on the crystalline moieties formed such that ion transport occurs macroscopically through these regions (surrounded by insulating charge barriers) as opposed to the molecular charge transport mechanism of lightly doped conducting polymers.

The level of crystallinity may also influence the color of the polymer. The reduced form (LEB-PANI) changes in color from colorless (or opaque) to dark blue can be attributed to the presence of partially crystalline regions due to the polymer's ease of oxidation in air.[21,22] Commercial LEB-PANI powders can be found with these characteristics. As the oxidation level and doping level increases, the level of crystallinity or chain ordering also increases and the pigmentation traverses from dark blue to dark green.

Conducting polymers, such as polyaniline, are termed ***"disordered semiconductors***." That is because, during doping, an electron is removed from the "top of the valence band" and excited to a higher transition, the highest of which being a transition to the conduction band. Many researchers have idealized the band theory of inorganic semiconductors such as Si and GaAs to describe doping effects and the basic electronic conduction properties of ICPs. Alternatively, the valence and conduction bands in inorganic semiconductors translate to π or bonding and π^* or anti-bonding bands in conducting polymers, respectively. Electrons (π electrons—electron from π^* bond created between two atoms in a conjugated system, i.e. C=C, C=N, C=O) can nucleate through the conjugated system via the π bonds (C=C consists of 1 σ bond and 1 π bond, the latter of which needs less energy to break) between C and N and C and C (for polyaniline). Once this happens, the charge is said to be excited from a lower energy (bonding molecular orbital) to a state of higher energy (anti-bonding molecular orbital) within the molecular matrix. Once excited, the electron can be easily removed (i.e. by an oxidizing gas).

During doping (looking at π doping for simplicity) distortions formed along the polymer chain translate to intermittent states (localized electronic states) within the band gap to which electrons can transition to once excited from the π band. This results in distortion of the highest occupied molecular orbital (HOMO) upward and relaxation of the lowest unoccupied molecular orbital (LUMO) downward within the band gap. These localized states can be conceived as the polarons and bipolarons formed within the physical structure of the polymer. The electronic states created just below the π^* band and just above the π band remain completely empty and completely full, respectively until an electron is excited. It should be noted that electrons once transitioned to these mid-gap states can be removed and excited from these energy band to higher energy bands. Polaronic bands are formed initially and if further electrons are removed (from the polaron as well as the band) the formation of bipolaronic bands transcends. With further doping, the electronic states can coalesce into new electronic bands. The result is a smaller band gap (electronic bands move closer to the Fermi energy) and evolution of the polymer from an insulator to an organic metal transpires. *The width of electronic band gap in polyaniline ranges from 3.6 eV for leucoemeraldine to 1.4 eV for pernigraniline*.[23]

Both the polarons and bipolarons act as charge carriers for delocalized electrons to tunnel through the monomer units inducing a flow a charge along the polymer chain. Physically polarons are delocalized charge carriers and bipolarons are localized charge carriers, with the former being the more energetically favorable defect.

Figure 2 illustrates that, with continued doping, localized states formed in the band gap (polarons and bipolarons) transcend the molecular orbitals from higher energies to lower energies. The polarons and bipolarons eventually coalesce into the π and π^* bands.

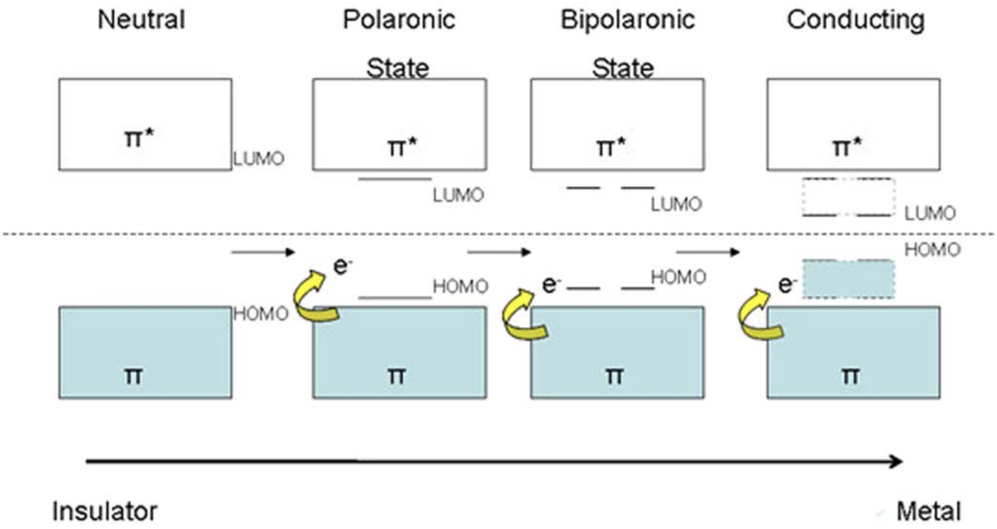

Figure 2. Band Theory evolution of polyaniline from insulating to metallic regime.

The electronic transitions are observable by spectroscopic techniques such as ultraviolet visible (UV–vis) spectroscopy. During this analysis, ultraviolet light absorbed by the material irradiates the molecules in the polymer structure inducing photochemical reactions which excite electrons to different energy states. This technique can be proven valuable for determining the extent of conjugation, the oxidation level,[24] and dopant effects on the conformational structure of the polymer.

In the presence of gases, in polyaniline, both redox and protonating/deprotonating conduction mechanisms are activated enabling the use of this material as a gas sensor. Interactions between the surface of polyaniline and the adsorbate may induce further doping/de-doping of the polymer resulting in an increase or decrease in electrical resistance.

During gas sensing, the polymer can exhibit swelling due to absorption of the analyte, but more importantly *the analyte molecules can adsorb and react with active sites* along the molecular structure of the polymer inducing conformational and electronic changes in the polymer that translate to a change in the films' electrical resistance. These changes can also be manifested as optical, physical, chemical, electrochromic, or magnetic changes in the polymer.

Researchers have employed diverse techniques for chemically and physically alter the structure of polyaniline, in an effort to enhance the selectivity and sensitivity of the polymer to analytes such as CO_2, CO, SO_2, NO_2, and NH_3.

Dopants.—Researchers have observed that polyaniline hybrids with insulating polymers show enhanced structural and electronic stability in different gas atmospheres. The insulating base polymers employed enhance the overall reaction and adsorption kinetics of the hybrid by acting as adsorbents for the gas, and filters for interferents. The choice of matrix polymer depends on the stability of the polymer in varying gas atmospheres, vapor transport ability, and affinity of the polymer to the encapsulated material. Several matrix polymers commonly employed are poly (vinyl acetate),[25] poly (vinyl alcohol),[26,27] poly (methyl methacrylate),[28] and polystyrene.[28] Solution and powder blending of polyaniline with these base polymers are common routes employed in enhancing the processibility of polyaniline for sensing applications. Charge transport in these polymers is dependent on the concentration of polyaniline and morphology of the matrix composite.[2] The transition of the composite from insulating to conducting occurs with an increase in the concentration, doping, and oxidation level of the conducting filler, polyaniline. A decrease in percolation length between neighboring particles corresponds to the increase in polyaniline concentration. This affects hopping and/or tunneling mechanisms of the electron as it traverses from $\pi \rightarrow \pi^*$ and from one conducting grain to the other.

Other efforts to enhance the sensitivity and selectivity of polyaniline include impregnated polyaniline with nanoparticles, such as carbon nanotubes,[29] SnO_2,[3] TiO_2,[3,30] In_2O_3,[31] Fe–Al,[32] Ni,[33] Au,[34] Nafion,[34] and zeolite[35] to form specific binding sites for chemical interactions. The inorganic nanoparticles implanted in the polymer matrix catalyze the reactions between the polymer and the gas resulting in an improvement in response time as well as an increase in the overall electrical conductivity of the film.

Novel dopants employed include poly (4-styrenesulfonate-co-maleic acid) for templating and synthesizing for NH_3 detection,[36] maleic acid for CO detection,[29,35] and acetic acid[37] for NO_2 detection.

Deposition techniques.—One major factor influencing sensitivity is the dispersion quality of polyaniline in the sensor matrix. The more dispersed the polyaniline powders, the better the diffusivity of the gas agent into the polymer matrix yielding enhanced film sensitivity. A primary factor that may influence the dispersion quality is the deposition technique employed. Typical polyaniline deposition techniques include electrochemical deposition, spin coating, dip coating, and drop-coating.[34] Some of the newer and innovative methods include self-assembly,[3,4,31] templating, Langmuir Blodgett,[37] and thermal[38] and vacuum evaporation.[32] Most novel techniques involve in situ polymerization (chemical or electrochemical) of polyaniline on the transducer (yielding high surface area nanofibers)[4,39,40] or nanoparticles seeded into the polymer matrix.[3,29,31–34]

Table I lists the typical processing of polyaniline-based environmental gas sensors. Dopant choice can influence the overall sensor response to target analytes. Researchers have also seen that hybrid polyaniline composites with insulating polymers have improved structural and electronic stability in different gas atmospheres, which improves the overall reaction and adsorption kinetics by acting as adsorbents for the gas and filters for the interferents. Deposition processes are also listed in Table I, as the deposition quality heavily influences the sensitivity of the gas sensor. By manipulating its microstructure, polyaniline has demonstrated suitability as a gas sensor.

Researchers have shown that through manipulation of polyaniline's microstructure via novel processing and synthesis techniques, as described above, polyaniline becomes a suitable candidate for gas sensing applications. Many of the mentioned systems employ the emeraldine base or salt form of polyaniline for gas detection. Leucoemeraldine base polyaniline was found, in our previous work, to be selective to NO_2 detection due to its oxidation sensitive structure (the benzenoid amine structure are vulnerable to oxidizing species like NO_2).[41]

Future Needs and Prospects

Leb polyaniline-cellulose acetate hybrids for breath and skin-gas sensing.—Cellulose acetate (CA) has been employed widely for filtration and reverse osmosis.[42–44] This natural polymer has also

Table I. Typical Polyaniline Sensor Deposition Techniques.[41]

Deposition/Processing Technique	Dopant/Composite	Gases	Detection Limit	Response Time
Spin coating[36]	Poly (4-styrenesulfonate-co-maleic acid)	NH_3	5ppm	60 s
Langmuir Blodgett[37]	EB/Acetic Acid	NO_2	20ppm	10 s
Cyclic Voltametry[34]	$HClO_4$, H_2SO_4 HCl/PANI/Au/Nafion	NO_2	20ppm	18 min
Constant Current[34]	$HClO_4$, H_2SO_4 HCl/PANI/Au/Nafion	NO_2	20ppm	19 min
Constant Potential[34]	$HClO_4$, H_2SO_4 HCl/PANI/Au/Nafion	NO_2	20ppm	14 min
Interfacial Polymerization[40]	HCl	NO_2	10ppm	104 s
Solution Casting[27,29]	EB/ Polyvinyl Alcohol composite; maleic acid/carbon nanotubes	CO_2/CO	100ppm/ 167ppm	5 min/0.6 min
Self Assembly[3,4]	HCl/SnO_2, TiO_2; aminosilane for templating	CO/NH_3	1 ppm/0.5ppm	80 s/60 s
Drop Cast[31]	Camphorsulfonic acid (CSA/In_2O_3)	CO/NO_2	60 ppm/ 0.51ppm	24 s/30 s
Vacuum Deposition[32]	Fe–Al	CO	10ppm	5 s
Pressed Pellets[35]	Maleic acid/zeolite	CO	7.8ppm	169 min

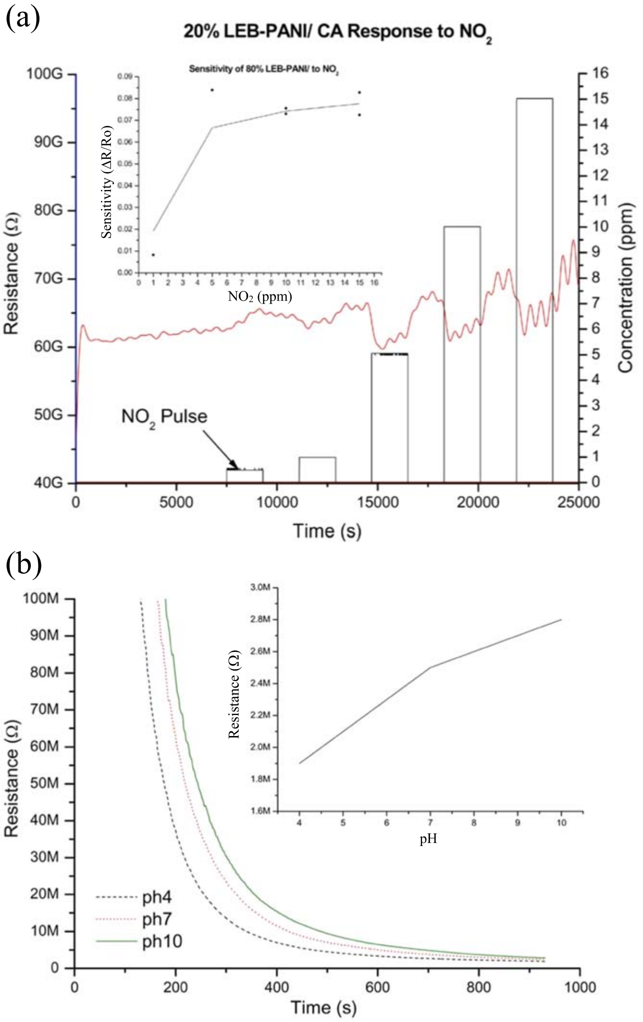

Figure 3. (a) Sensor response of LEB-PANI/CA hybrid to NO$_2$ at 20% humidity[59]-the red line indicates resistance change for different pulses of NO$_2$; (b) Response of ES-PANI/CA hybrid with time for variable pH values; and changes in the resistance for different pH values at the given time (see inset).[59]

been used as a support matrix for dissimilar materials (i.e. conducting polymers, ceramics, metal nanoparticles, etc.,). CA is traditionally produced by reacting the polysaccharide cellulose, $C_6H_{10}O_5$, with acetic anhydride $(CH_3CO)_2O$, which when hydrolyzed yields acetic acid. The transport properties of CA have been studied for applications ranging from wastewater treatment,[45] chromatography,[46] and biotechnology.[47] For conducting materials (i.e. ICPs, carbon nanotubes, metal oxides), it has shown to provide adequate pathways for charge transport within the composite matrix, yielding it to be a suitable base matrix for sensing and applications.

For polyaniline, CA can be employed as a hole transport layer.[48–55] The advantage of electrospun CA is that it is water repellant and more structurally stable against high levels of humidity. The water susceptibility of the polymer is dependent on the degree of substitution of acetyl groups (40% for CA employed in our earlier studies). Since *CA is not soluble in water*, hybrids of CA and LEB-PANI retain their morphological character even after repeated exposures to humidity. CA can act as an oxidant for LEB-PANI. In our earlier work,[41] FTIR analysis of 20:80 lEB PANI:CA mats showed characteristic bands around 1600 cm^{-1}, which suggests the presence of quinoid structures in polyaniline. Several bands around 1500 cm^{-1} suggest the formation of bipolaronic structures. These peaks represent protonated imine species with oxygen anions. Thus, the acetate groups of CA may have disassociated and became bound to N sites along the LEB-PANI chain inducing the formation of these localized charge carriers.

PANI/CA sensors.—FTIR of the CA LEB-PANI composite processed using acetone and or acetic acid as solvents reveals bonding between the acetate groups of CA and the benzenoid and quinoid rings of the polymer as well as at the imine N centers of LEB-PANI. It also shows several bands relative to the vibrations of the $C=N^+O^-$ structure. These groups can form from the interactions between CA and LEB-PANI or acetone and LEB-PANI giving rise to O^- anions. Acetic acid may disassociate into COO− and H^+ or liberate a hydroxide or O^- which can bind to various sites along the LEB-PANI chain.

XPS analysis further suggested that LEB-PANI transformed into a higher oxidation state, as evidenced by the reduced intensity of the −NH− peak at 399.6 eV. Although the matrix lacks in neutralized amine sites, the peak at 400.6 eV suggests that many of these sites have been protonated or transformed into polarons. Other workers[56,57] claimed that the peak at 400.6 reflects $>C–N^+$ structures while the peak at 402.4 eV reflects $>C=N^+$ structures. The rise in the number of protonated amines may be a consequence of protonation of quinoid imine units yielding N^+H through internal redox processes, protonation of the neutral amine structures by the acetate groups of CA, or polaron formation via reactions (protonation/oxidative doping) between the acetate groups of CA and LEB-PANI. The peaks at 288.8 eV and 286.8 eV reflect the cellulose acetate groups in the composite which are responsible for the molecular modifications in LEB-PANI leading to the higher oxidation state and slightly doped structure.

LEB-PANI-CA sensors (see Fig. 3a) are operable at various levels of humidity making them suitable for breath and skin gas analyses. It has been demonstrated that pH found in human breath condensate correlates to certain gas constituents of exhaled breath.[41] The advantage of measuring pH is related to the decomposition or mixing of gaseous biomarkers resulting in false positives and ambiguity in sensor response. The pH of the condensate has been shown to be directly related to the acidity of airway surface liquid which changes with an increase in oxidative stress associated with certain pulmonary diseases.[58]

Conductimetric hybrid systems consisting of cellulose acetate and ES-PANI were fabricated in our earlier research using the electrospinning technique—see Fig. 3b.[59] These were used for "headspace analyses" of solutions containing different pH levels.[59] Results from preliminary sensing tests with pH buffer solutions ranging from 4 to 10 reveal that as the pH increases, thus decreasing $[H^+]$, the films exhibit an increase in resistance by $1.7–2.0 \times 10^{-7}$ per pH unit (which correlates to a tenfold decrease in $[H^+]$). This increase in resistance is associated with a reduction of the electroactive sites along the polymer chain by the basic headspace. As $[H^+]$ increases, the films become highly protonated along the imine sites yielding a decrease in the film's resistance on exposure to the headspace of lower pH. The CA ES-PANI fiber composites are shown to be promising candidates for this application. Future studies should focus on developing volatolomic probes and skin sensors targeting the pH levels in the range of 7–8 which represent the deaerated exhaled breath condensate of healthy people and people inflicted with illnesses such as bronchitis, asthma, and chronic obstructive pulmonary disease).

Recently, there has been an increased interest in exploring PANI electrochemical sensors[60] and PANI/CA mechanochemical skin gas sensors,[61] both for wearable devices. The versatility in the transduction modes in sensing makes PANI superior to the other conducting polymers.

Conclusions

Polyaniline has been extensively studied and employed for various sensing applications. The responsive nature of polyaniline

(PANI) is highly dependent on the processing conditions, film composition, and morphology. The mechanisms employed in producing PANI films for chemical or biological sensing applicationsn dictate the material's electrical conductivity, overall structure, and stability. Hybrids of LEB PANI with CA are presented here as the next generation of room temperature gas sensors for disease biomarker detection.

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