CHEMICAL REVIEWS

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Chem. Rev., **2008**, 108 (2), 746-769 • DOI: 10.1021/cr068112h

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Chemical Reviews is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

746 *Chem. Rev.* **2008,** *108,* 746–769

Composites of Intrinsically Conducting Polymers as Sensing Nanomaterials

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Received August 10, 2007

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1. Introduction

Composites of intrinsically conducting polymers (ICPs) are materials that utilize conjugated polymers and at least one secondary component that can be inorganic or organic materials or biologically active species. The goal is to produce a new composite material that has distinct properties that were not observed in the individual components. This may include either new or improved chemical properties that can be exploited for chemical or biological sensing. For example, adding carbon nanotubes tends to drastically influence the electrical and thermal conductivity of ICPs. A secondary aspect concerns the stabilization of the secondary component in the polymer matrix. Enhanced optical, electrical, or mechanical properties such as stiffness and strength are common. In some cases, the physical and chemical properties of the secondary component are much different after composite formation. For the purpose of this review we will primarily focus on the ICPs such as polyaniline, polypyrrole, and polythiophene and their derivatives. The resonance-stabilized structure of ICPs allows, for example, incorporation of ions, nanoparticles, or nanowires of metals, metal oxides, carbon, or molecular species such as metallophthalocyanines or biologically active components such as enzymes, antibodies, and antigens.[1] In some cases, the ICP will simply act as a template for the incorporation of the secondary component. In that case, the secondary component will impart the chemical properties required for chemical sensing. In other cases the materials are linked through electrostatic interactions which influence the electronic and physical properties of the materials used to prepare the composite.

The combined physical/chemical properties of the components are exploited for chemical sensing when the materials are joined. Differences in the properties of composites containing similar components are often tied to the method of preparation. Therefore, preparation methods will be discussed in more detail with respect to the “how” the secondary component is incorporated in the ICPs. The major advantage of ICP composite materials over the ICP alone is based on the increase in active surface area and ability to form good electronic contact between the composite components and the transducer. The parent polymer provides high dispersion and high surface area for the secondary components to be integrated and creates templates for chemical reactions and interactions. The inherent stability and symbiosis between the two components used to create the composite material is often superior to the bulk components alone.

This review is organized as follows. First, we briefly summarize the properties and limitations of the most frequently used materials in chemical and biological sensors. Then different approaches to combine them with ICPs are discussed. The methods have been broadly classified as polymerization, dispersion, redox reactions, and electrostatic interactions. When applicable the strategies used to control the size, shape, and distribution of the secondary component in the composite are emphasized. When relevant the catalytic applications of the composite materials are examined. The advantages of using these composites as sensing material can be expressed with respect to increased surface area, higher numbers of analytical recognition sites, lower detection limits, low resistivity or faster response times, and improved environmental stability. The mechanical properties of the material are often improved which leads to more robust sensors.

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10.1021/cr068112h CCC: $71.00

David W. Hatchett received his B.Sc. degree from California State University, Stanislaus, in 1992. He received his Ph.D. degree from the University of Utah, Salt Lake City, in 1997 for work on the electrochemical formation of sulfide and thiolate monolayers on Ag. Dr. Henry S. White supervised this work. After graduation he accepted a postdoctoral associate position in the Department of Chemistry in Professor Jiri Janata's Group at the Georgia Institute of Technology. His postdoctoral research focused on the sensing properties of polyaniline (PANI) and the acid doping and control of species in conductive polymer membranes. His current research interests are diverse including the chemical and electrochemical synthesis of PANI/metal composites of PANI/Au, PANI/Pt, and PANI/Pd. The primary goal of this research is to produce composite materials with unique sorption, chemical, sensing, and catalytic properties. In addition, composite ion- and gas-selective membranes for chemical sensing applications are examined. His research focuses on the development and testing of gas- and ion-sensing materials that can be used to manufacture chemical sensors. Finally, electrochemical characterization of lanthanide and actinide species in room-temperature ionic liquids (RTILs) has been explored. This work examines the potential-mediated separation of species using the large potential window provided by nonaqueous RTIL systems. The range of materials produced and characterization of the materials are examined with respect to defined and diverse applications. His research provides insight into the rational design of materials for chemical sensing, catalysis, ion transport, and sorption processes.

In summary, the aim of the review is to explore a fundamental and technological incentive for ICP composite sensors, the sensing properties, and how molecular ICP composites are made. The behavior of the secondary component relative to the primary component and how the combined properties of the composite improve sensing applications is also examined. The references selected in the text do not reflect the chronology of the advances in the research field within the last 7 years, and we do not claim to present every possible reference for completeness. Rather the references are meant to highlight specific aspects and applications that are important in the synthesis and application of ICP composite to chemical and biosensors.

2. Properties and Limitations of Composite Components

2.1. Intrinsically Conducting Polymers (ICP)

In general, intrinsically conductive polymers (ICPs), also referred to as organic semiconductors, are polymers with a delocalized π-electron system with an "intrinsic" wide band gap that defines their affinity for electrons (work function).[2] They are good candidates for developing chemical or electrochemical sensors for two reasons: (1) The electronic conductivity, related to the redox state (doping level) of a conducting polymer, is modulated by the interaction with various analytes resulting in changes in parameters such as resistance, current, or electrochemical potential/work function. Since the ICP acts as an electronic transducer, the magnitude and rise of the electrical signal correlates with the type of physical−chemical interaction involved in the signal generation. The interaction with analytes introduces changes in the physicochemical properties resulting from structural reorganization of the polymer chains. These changes are facilitated by an increase or a decrease of the density of charged species through polymer/analyte interaction or hydrogen bonding between the species.[3] (2) They are attractive as sensing layers because they retain processing properties of polymers, lowering manufacturing costs of films, powders, or wires. The processing of ICPs, that are of poly(heterocyclic) types, such as polypyrrole (PPy), polyfuran, polythiophene (PT), poly(*p*-phenylene vinylene), aromatic poly(azomethine)s, and polyaniline (PANI), from solution or using heat treatment has been reviewed with emphasis on the design of dopant, special catalytic properties, and special optical or spectroscopic properties.[4] Consequently, specific functionality can be added to the ICP matrix by entrapment during the polymerization process.

Mira Josowicz studied chemistry at the Politechnika Slaska, Gliwice, Poland, where she graduated in 1966 in Physical Chemistry. She received her Ph.D. degree from the Technical University in Munich, Germany, in the field of Inorganic Chemistry with Professors Ch. Quentin and H.-P. Fritz. From 1983 to 1986, she was a Feodor-Lynnen-Humboldt postdoctoral research fellow at the University of Utah with Professor J. Janata. After her return to the University of Bundeswehr in Munich, she finished her habilitation in 1992 in the field of chemical sensors. From 1992 to 1997 she was a staff scientist in the Materials and Chemical Sciences Center at the Pacific Northwest National Laboratory, Richland, Washington. Since 1997 she has been Principal Research Scientist in the School of Chemistry and Biochemistry, Georgia Institute of Technology. Her main research interests include chemical sensors and properties of organic semiconductors.

Charge carriers are introduced into the polymer by doping, which can be accomplished chemically, electrochemically, or optically.[5] For example, polyaniline can be protonated by triflic acid generated by UV photolysis of triphenylsulfonium triflate salt.[6] The strong acid, such as triflic acid or tetrafluoroboric acid, lowers both the work function and increases the conductivity of polyaniline (PANI) base according to the known proton doping mechanism. In contrast, addition of triflate salts to the emeraldine base form of PANI in the solid state leads to formation of localized states that do not contribute to the conductivity but lower the work function of the polymer.[7] We call this form of doping charge-transfer doping as opposed to oxidative and proton doping. This distinction has important implications for use of PANI in various types of sensing device structures. When PANI is used as the replacement for the metal in the insulated gate field-effect transistor the value of the work function is critically important because it controls the threshold voltage. Since there is no current passing through the PANI layer in such a device, its conductivity is irrelevant. However, when PANI itself is used as a conductor of electronic current, the type of doping that leads to conductivity changes is important. Moreover, in some devices, such as thin-film transistors, both charge transfer and proton doping play a role in the operational characteristics of the device. Furthermore, the conductivity of ICPs depends on its ability both to transport charge carriers along the polymer backbone and to hop between polymer chains.[8] The work function of the ICP is defined by its redox state and the basis for modulation of optical transitions and ionization potential.[9] The environmental stability of the material is crucial for analytical calibration of the sensor. It has been demonstrated that the functional groups of camphorsulfonic acid used as a dopant for PANI can actually help to fulfill such requirements.[10]

Intrinsically conductive polymers have advantageous morphological and structural properties that are critical to the sensitivity and selectivity of gas or ion sensors. These properties are sensitive to polymerization parameters such as the type of the counterion, supporting electrolyte, and solvent monomer/counterion concentrations. Introduction of subtly different dopant groups into ICPs including variations in doping level results in different conductivities of the material. Upon exposure to gases or analytes the ICPs show significant differences in conductivity responses due to changes in charge mobility and the amount of charge doping in the films. Selectivity of ICPs has been demonstrated through addition of a functional group to the precursor monomer or/and copolymerization to produce different ICP precursors. For example, the sensitivity to alkali-metal ions has been introduced by addition of polyalkyl ether or crown ether functionalized groups to the parent polymer chain. Furthermore, mixing pyridyl-based ligands with the parent polymer produces coordination sites. Introduction of metal ions can introduce conformational changes in the ICP that govern optical or electrochemical signals upon exposure to chemical or biological analytes. When the ICP is polymerized in the presence of a chiral compound, molecular-size specificity can be incorporated in the matrix. All of these possibilities were discussed in much more detail in a previous review by Swager et al.[11] Different synthetic routes and their effect on the gas sensing properties of ICPs have also been the subject of several reviews.[12]

The sensing mechanism, configurations, and factors that affect the performance of gas sensors fabricated using conducting polymers such as polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT) as the active layers have been reviewed by others within this issue of *Chemical Reviews*. In brief, the interactions of ICPs with ambient gases can be monitored using the membrane as a chemical resistor (conductivity changes), diode or field effect transistor (work function changes), optical waveguide (absorption changes), or surface acoustic devices (mass change). Since changes in work function are based on formation of a charge-transfer complex between the gaseous species and the conducting polymer,[13] methods for a stable and adjustable primary doping of the ICPs are necessary.[14] Electron donation or withdrawal by the analyte vapors leads to conductivity changes in the sensor films. A systematic study of the steady-state electrical resistance responses of alkyl-substituted polypyrroles (PPy) and a polyalkylterthiophene (PAT) doped with a variety of counter anions to volatile organic chemicals (VOC) comprising alcohols, esters, aromatics, and alkanes revealed a linear correlation between vapor concentration producing a fixed amplitude of sensor response with respect to analyte-saturated vapor pressures.[15] It has also been observed that the sensor sensitivity toward an analyte can be correlated with the differences in analyte polarity. Changing the dopant ion in the conducting polymer has a large effect on absolute sensor sensitivity but does not markedly affect the relative sensitivity toward different analyte functional groups. Humidified carrier gas depresses sensor sensitivity, suggesting competition between water and gas molecules. Polymer swelling based on humidity also implies that the pathways become saturated with water, which would then change the diffusion rate of the gases into the polymer matrix. Activity coefficients for solutions of organic vapors dissolved in conducting polymers are not available in the literature. Overall, a nonspecific partition model of conducting polymer interaction with organic vapors is proposed in which, for a given analyte functional group, the electrical resistance transduction mechanism is insensitive to large variations in analyte size and shape.

Furthermore, conducting polymers are useful as both ion-to-electron transducers and sensing membranes in solid-state ion-selective electrodes. However, the influence of ambient media such as oxygen, acids, bases, redox reactants, water, and organic vapors on changes of the polymer structure, composition, and degradation should not be overlooked. The benefits and disadvantages of such processes for analytical characteristic of polypyrrole-based electrochemical sensors have been reviewed previously.[16]

The physical properties of ICPs can also be a hindrance for certain applications and must be considered when choosing which polymer will be used. For example, in bioelectrochemical applications it is important that the polymer film remains conductive at pH values higher than 4. The conductivity of PANI is reduced as the pH is increased, leading to a decrease in proton doping. However, the conductivity of ICPs such as polythiophene or polypyrrole demonstrates very little pH dependence. In addition, the effect of counterion incorporation into the polymer as a dopant during polymer synthesis or testing on the pH stability of the ICP can also be important.[17]

In some cases the lack of proton or anion doping can be used to create sensor membranes. Specifically, the physical properties of undoped conjugated polymers where the band gap depends on chemical constitution of the conjugated backbone and the nature of the substituents attached to the main chain have been exploited as electroluminescent (diode) sensors. The luminescence generation is caused by excitation that occurs during interaction of the polymer with the analyte.

The wide variety of chemical sensors produced from ICPs demonstrates the diversity of the material. The progress in development of potentiometric sensors based on the use of ICPs within the last 5 years has been reviewed.[18] Optical chemical sensors based on the electrochromic properties of ICPs have also been reviewed in this issue and by others.[19] Although these reviews focus on the sensing properties of ICPs only, incorporation of secondary materials with ICPs to produce composite materials provides another approach for producing diverse sensing materials with higher chemical stability and improved analytical selectivity.

2.2. Carbon-Structured Materials

The chemistry and physics of carbon nanotube (CNT) have been the focus of a large number of studies. The enormous development of the carbon structures in recent years can be attributed to the high electrical conductivity, high chemical stability, and extremely high mechanical strength and modulus. All of these properties can be exploited to develop a new generation of chemical sensors.[20] One significant drawback to the use of CNTs in sensors remains their lack of chemical selectivity. Selectivity is minimal due to the fact that the response mechanism is based on the electron affinity and density ratio of the target analyte relative to the CNT transducer. Therefore, formation of ICP/CNT composites is important and functionalization is critical for use in chemical sensors.

CNTs are used in composites because they can be treated as inorganic or organic reagents based on their inherent “graphene” structure. They have electron-transport properties consistent with π-conjugated systems with metallic or semiconducting properties depending on their diameter.[21] The rolled graphene structure forms single-walled nanotubes (SWNT) that can be then treated as one-dimensional conductors.[22] They have great potential for conductance- and capacitance-based sensors because they are sensitive to changes in dipole moment and polarizability of the adsorbate when charge-transfer complexes are formed between adsorbates and the SWNT.[23] The difficulty associated with the assembly of SWNTs has led to the use of SWNT networks that contain a large number of randomly positioned nanotubes (bundles). Consequently, the properties of SWNT devices depend on the position, number, and electronic type of its constituent nanotubes. A wide number of synthetic conditions are currently used to produce SWNTs, but none of the parameters discussed can currently be controlled with a high degree of reproducibility. The key to the electronic quality of random networks of SWNTs is the electrical contact that is formed between intersecting structures. SWNTs adhere to surfaces such as SiO_2 via van der Waals forces that deform the SWNTs at the point of intersection and pull them closer together. The proximity of the two structures increases the probability of internanotube tunneling.

Multiwalled nanotubes (MWNT) are based on a concentric tube within a tube and can have either metallic or semiconducting characteristics.[24] These electrical hybrid tubes can be expected to behave as metallic nanowires due to the average current density across the characteristically different walls. In addition, wall-to-wall conduction is possible within the MWNT, allowing the properties of the metallic MWNTs tubes to dominate charge transport. Some researchers have reported that MWNTs behave as diffusive conductors.[25]

The principles for CNT gas sensors for the detection and quantitation of gases are based on changes in electrical properties induced by charge transfer with the gas molecules or changes in the adsorption.[26] The ability of the adsorbate to transfer charge depends on the electron affinity of the adsorbate with respect to the CNT. For example, the conductivity of the semiconducting SWCNT upon exposure to 200 ppm of NO_2 (electron-withdrawing gas) changed within 10 s, up to 3 orders of magnitude. In contrast, the conductivity decreases by 2 orders of magnitude upon exposure to 1% NH_3 (electron-acceptor gas) within 2 min. In principle, the response mechanism can be applied to many other electron-accepting or -donating gases (NO, CO, CO_2, etc.). However, a major obstacle in manipulating the electron affinity of CNTs is their limited solubility in solvent. They have a tendency to “rope up” or aggregate in solutions rather than dispersing uniformly.[27]

Aggregation of CNTs is typically minimized through chemical modification. For example, introduced carboxyl groups enable covalent coupling of molecules through the creation of amide or ester bonds. High solubility in organic solvents can be obtained by covalent or ionic attachment of long-chain aliphatic amines onto the carboxyl groups. The presence of the “modified” carboxyl groups leads to reduction of the van der Waals interactions between the CNTs, allowing separation and further chemical functionalization in aqueous or organic solutions. Functionalization also provides an effective tool to broaden the spectrum of electroanalytical chemical sensing and electrochemical biosensing applications of CNTs through subsequent solution-based chemistry.[28] These modifications also allow secondary aspects to be tailored including electronic and mechanical properties.[29] High solubility in water solution was achieved through carboxyl-based coupling of hydrophilic polymers such as poly(ethylene glycol) (PEG).

Use of CNTs as transducers in chemical and physical processes after functionalization is also possible. Functionalization of the CNTs can be conducted in a controlled and selective manner electrochemically, where an active radical is generated from a target reagent present in solution, resulting in polymer formation on the CNT. Attention has been directed also to electron-donor−acceptor molecules such as ferrocene and phthalocyanine because they can act as secondary chemical transducers in electrochemical processes. Finally, functionalization of SWNT with zinc−phthalocyanine (ZnPc-SWNT) results in a photoinduced electron-transfer effect that has potential to be exploited in optical sensors.[30]

Significant progress in interfacing carbon nanotubes with biomolecular materials was made in key areas such as aqueous solubility, chemical and biological functionalization, biocompatibility, and specificity with respect to the electronic sensing properties of proteins.[31] Development of hybrid nanostructures using MWNTs has been realized via adsorption of protonated amino groups that are able to anchor gold nanoparticles using electrostatic interactions. Functional species can then be affixed using the well-known mechanism for thiol sorption at gold surfaces.[32] Recent advances in the asymmetric end functionalization of CNTs, with two different building blocks, allow a variety of materials to be produced. The end groups can be used to control hydrophobicity and hydrophilicity, ion transport through the CNT channels, and photoinduced electron transfer between donors and acceptors. Both approaches show great promise in the rational design and realization of a host of new chemical sensing materials.[33]

Despite the fast response of CNTs to low-vapor-pressure analytes, their long recovery time, extremely high affinity to adsorb oxygen, and complex fabrication process still remain a major drawback to their use as sensing materials. The homogeneity of the materials suffers due to inadequate separation procedures for fractionation based on conductivity, length, and diameter. Therefore, the low reproducibility of the physical properties has a major impact on the quality of the response and understanding of the mechanisms. Furthermore, electrical properties of the contacts often dependent on the geometry and external factors such as ambient light are not well understood. In contrast, the conductivity of most ICPs is lower than that of the CNTs and is well defined.

2.3. Metals and Metal Oxides

Metals in “nano” form exhibit unique properties relative to bulk metals. For example, gold nanoparticles change color and are very good catalysts relative to the bulk material. In addition, nanoparticles act as semiconductors, and their melting temperature decreases.[34] Material clusters of nanoscale diameter often exhibit structural, electronic, spectral, magnetic, and chemical characteristics that are unique to the size regime. These properties cannot be easily extrapolated or deduced through scaling arguments based on the knowledge of these properties at the bulk limit.[35]

A number of approaches have been demonstrated for the synthesis and assembly of metal nanoparticles. Examples include two-phase synthesis of monolayer-protected nanoparticles, stepwise layer-by-layer construction, DNA complimentary binding, polymer- or dendrimer-mediated assembly, and mediator-template assembly.[36] Supported metal particles were also grown in the liquid phase and then deposited on a substrate or formed directly on a surface from a solid−liquid interfacial layer.[37] The particle size can be controlled most efficiently using sol deposition methods or zeolites, where the metal component is introduced and retained within the pores. However, problems can arise with regard to the stabilizing agent that maintains the particle in solution. Stabilization of the particles inside the pores through complexation can also occur. Use of metal carbonyl clusters to produce precursors of the nanoparticles seems to be least efficient regarding the difficulties in size regulation.

Understanding the basis of the fundamental variations in the physical−chemical properties of materials ranging from the molecular level to solid-state chemistry has a great impact on organic, coordination, and solid-state chemistry, catalysis, physics, and materials science. Extensive studies are currently being performed that attempt to correlate the material properties with cluster size. In addition, factors that influence the surface properties with respect to catalysis and optical properties of nanomaterials are of general importance.[38] The published knowledge of the frontiers of cluster science extends rapidly and is a topic of several books and several hundred publications.[39] Topics related to metal clusters at surfaces have included the synthesis and assembly of nanocrystals, theory and spectroscopy of inter- and intraband optical transitions, single-nanocrystal optical and tunneling spectroscopies, electrical transport in nanocrystal assemblies, and the physical and engineering aspects of nanocrystal-based devices.[40] An overview of the structure and resulting electronic and optical properties of metal nanoparticles embedded in insulating polymer matrices with emphasis on preparation of such materials have been reviewed with a focus on thin film deposition techniques.[41] A general introduction to nanoscience based on the synthesis of colloidal nanocomposite particles and their use in making metal−nanoparticles such as silver, iron, ligands shell, inorganic core, oxide shell, semiconductor nanocrystals, nanorods, nanotubes, nanobelts, etc., has also been presented in a review recently.[42]

The long-term stability of these superlattices depends on the method used for their stabilization. It was reported that thiol-derivatized Au clusters are stable in toluene for over a 3-year period. When the particles are allowed to crystallize under ambient conditions, the protective alkanethiol coating slowly degrades. Under these conditions it becomes energetically favorable for the Au particles to minimize their surface energy through aggregation.[43] The larger particles (∼8 nm diameter) destabilize at a much slower rate than the smaller ones (∼4 nm). The reason for the decreased stability of the smaller particles as compared to the larger ones is possibly related to their geometrical structure. It was observed that heating of nanoparticle arrays of different sizes at different rates introduces instability into their array structures. That instability is initiated by the smaller nanoparticles that have a tendency to melt first. By melting a string of nanoparticles it is possible to produce a wire that is 10 times thinner than any wire made using the standard microelectronic process of electron beam lithography. The conductivity can be controlled by altering the size and separation between nanostructures that make the supercrystal.

The influence of size, shape, and surface chemistry of small metal clusters that are dispersed on a support is crucial to understanding their electronic structure.[44] The intrinsic properties of the cluster are nonscalable from bulk analogues for the reduction of the particle size to only a few dozen atoms. For example, gold reduced to clusters of eight atoms on an appropriate support transformed into an efficient, active center for oxidation of CO. The book *Nanocatalysis* recently published by Landmann and Heiz introduces the properties of nanosized materials and focuses on the influence and effect of dimensionality and size in the new and unique chemical properties.[45]

Use of gold nanoparticles in the field of sensing and recognition demonstrates that these nanoparticles are an ideal starting material for this purpose.[46] One of the most attractive features of monolayer-protected clusters (MPC) for sensor application is the ease of introduction of functional groups coupled to biomolecules. For example, thiolated oligonucleotide are attractive for the voltammetric detection of hybridized DNA targets, for encapsulation with conjugated carbohydrates for labeling of specific proteins, or coupled to antibody conjugates for detection of antigens. Furthermore, these MPC systems are good candidates for modeling recognition processes and development of new biomimetic catalysts because they have globular shape and size comparable to many biological molecules including proteins, nucleic acids, enzymes, and many cellular substructures. Some interesting examples of these systems have been recently reviewed.[47]

Functionalization of gold nanoparticles is also of general importance. For example, a soft shell of organic chains surrounding the Au core can easily be exchanged with different thiols present in solution. The exchange allows introduction of the desired (sensitive) functionalized thiols using a reaction that has been termed “place-exchange reactions”.[48] The “place-exchange reaction” is the macroscopic consequence of the dynamic self-assembled nature of the protective monolayer. Studies of the mechanism of the “place-exchange reaction” are still not conclusive, but the reported data suggest that an associative−dissociative process takes place. These processes suggest that the core Au particles may be converted to functional species with designed chemical structure and reactivity. More importantly, they provide the ability to tailor selectivity of the surface through thiolate bonding and exchange.

Bimetallic nanoparticles (bi-MNPs) containing two metals are of great interest since they can exhibit catalytic, electronic, and optical properties distinct from the corresponding monometallic nanoparticles. A number of approaches have been demonstrated for the synthesis and assembly of bimetallic or trimetallic nanoparticles.[49] More recently, the optical,[50] magnetic,[51] and catalytic properties of multicomponent metal particles have been examined.[52] For example, the composition of Au/Ag alloy nanoparticles can be varied by changing the salt ratio used during the bimetallic particle synthesis. The different mole ratios of metals both in and on the bimetallic cores has been utilized to manipulate colors and surface plasmon resonance bands.[53] The interaction of the bimetal with target analytes changes surface plasmon resonance and can be used in developing sensors. Stable magnetization reversal transitions at room temperature of Pt/Fe alloy particles as small as 4 nm has also been achieved.[54] The materials can act as electrocatalyst for methanol oxidation[55] and oxygen reduction.[56] Whereas the synthesis of the nanoparticles assembly has been studied in detail, the interparticle distance of the multicomponent nanocrystal surfaces is not fully understood. It has been reported that manipulation of the core composition and linker chain length could provide new opportunities for exploiting binary nanoparticle-structured sensing and catalytic properties.[57]

Metal oxides exhibit electrical behavior that can vary from electrically insulating (MgO, and Al_2O_3), wide-band semiconductor (TiO_2, SnO_2, ZnO, Ti_2O_3), to metal-like (V_2O_3, ReO_3, RuO_2) behavior. Some oxides have several stable oxidation states that are very important in surface chemistry. The oxidation state can control the types of defect that may be formed and the chemisorption that takes place at their surface when they are used as a sensing layer. Usually the process of electron exchange between the conductance band of metal oxides and the adsorbed species is fast. However, the chemisorption process of gases is governed by both surface and bulk properties, which can be slow for sorption and desorption.

Reduction of the bulk surface to nanometer or micrometer size is an approach for influencing both the electronic and sensing properties of the metal oxides. The identification and control of structural features of metal oxide cluster size are prerequisite for preservation of its electronic, optical, or magnetic properties. The formulation conditions, time, and temperature can be used to form nanocrystals, nanorods, nanowires, or even nanoparticles with controllable sizes. Classical sol−gel synthesis can be used to control parameters including the diameter and aspect ratio based on the hydrolysis and condensation of metal−halide or −alkoxide precursors in aqueous solution.[58] The reported CO gas sensing of single-crystalline one-dimensional (1-D) SnO_2 nanocrystals (rod, wire) with a controllable size indicates that the sensitivity can be correlated with the specific surface area of the nanocrystals.[59] In order to improve the crystalline arrangement of very small particles, the nonaqueous solution, halide, and surfactant-free synthesis routes were used to produce SnO_2, In_2O_3, Nb_2O_5, and perovskite nanopowders.[60] The oxides are in the form of nanostructured powders that are composed of single crystallites with minimal aggregation and an average size of 2−20 nm.[61] Growth of 1-D oxide nanomaterials such as ZnO, SnO_2, In_2O_3, Ga_2O_3, SiO_x, MgO, and Al_2O_3 with controlled microstructured and size using chemical vapor transport and condensation systems has been reviewed.[62] Porous networks of metal oxides provide high surface area relative to bulk structures. In many cases the void geometry afforded by the structure of the material provides enhanced uptake of species relative to the two-dimensional bulk surface.[63] The sensitivity of any device is enhanced due to the increased number of interaction sites associated with the three-dimensional structure.

Finally, the chemical and physical properties of nanostructured materials can be much different than those observed for the bulk materials. The conductivity of arrays of TiO_2 nanotubes was reported to be approximately 9 orders higher that of bulk TiO_2 surfaces.[64] The enhanced conductivity was explained in terms of increased surface area, defined stoichiometry, and a greater level of crystallinity than in multigranular oxides. These materials showed potential for reducing the instability associated with percolation or hopping conduction. It is possible to envision that chemical sensitivity will be greatly influenced by the chemistry taking place at the surface since for most semiconductor oxides nanowires the Debye length (measure of field penetration into the bulk) is comparable to the radius of the wire. Furthermore, the increased electron and hole diffusion rate to the surface of a nanostructure allows the analyte to be rapidly photodesorbed from the surface even at room temperature. This implies that surface photoinduced redox reactions occur rapidly and interfacial charge-transfer rates are not limiting. Use of photoinduced desorption of a sorbed analyte for rapid detection is conceivable. Photoassisted desorption will increase the conductance of the nanowire, providing signal transduction for the sensor. Therefore, nanostructures of metal oxides show promise in improving the efficiency of electrochemical and optical sensing devices, encompassing a broad range of applications.

Studies have shown that TiO_2 nanotubes fabricated by electrochemical anodic oxidation exhibit a highly ordered structural morphology that enhances the photocurrent and photocatalytic behavior relative to TiO_2 nanoparticle films prepared by the regular sol−gel methods.[65] In addition, incorporation of SnO_2 (2.5 nm particles) with TiO_2 (25 nm) showed an enhancement (1.5 times) in the photocatalytic activity compared to the pure TiO_2 for decomposition of gaseous 2-propanol and evolution of CO_2.[66] Although the role of dimension, morphology, and composition is clearly identified in the study, the overall recombination rate between electrons and holes is considered to be retarded by trapping the photoexcited electrons from the conduction band of TiO_2 by the dopant species (e.g., SnO_2).

In recent years it has become clear that the reactivities and thermodynamics of small transition-metal oxides clusters exhibit many fascinating and unique properties. Reactions and thermochemistry of small transition-metal cluster ions demonstrate that quantitative thermodynamic information concerning the stability and reactivity of small transition-metal clusters in the gas-phase provides an understanding of the their function as catalysts at the molecular level, which is applicable to the bulk-phase limit.[67] The role of the catalyst in chemical sensor applications is to lower the reaction barrier in metal oxides based on weakening the O−O bond through charge transfer.[68] A second possibility is to use systems that contain O atoms without the O−O bonds. The reactivity of transition-metal oxides with oxygen atoms bound only to the transition metal remains largely unstudied.[69]

The molecular understanding of environmental catalysis of metal oxide clusters and their reactions has been the subject of a review.[70] Newer investigations show how particular size-selected clusters of Fe_2O_3 can become a potential candidate for promoting NO reduction and CO oxidation. The systems may even become dual-task selfregulating systems for conversion of CO to CO_2.[71] Unlike the bulk metal oxide system, occupation of different MO orbitals is possible with small clusters, resulting in different ionic charge states. The combined theoretical and experimental study of $FeO_3^{\pm}$ with CO reveals that cation clusters are more efficient in lowering reaction barriers and facilitate catalytic conversion of CO to CO_2.[72] The importance of d-orbital aromaticity has recently become evident in metal oxide clusters, $[M_3O_9]^-$ and $[M_3O_9]^{2-}$ ($M = Mo, W$). They are unique in that they involve a single fully delocalized metal–metal bond and may exhibit novel chemical, electrochemical, and catalytic properties.[73] More recently it has become clear that the cluster activity depends on the number of atoms, geometrical structure, and sorption site at which adsorption of the gas participates.[74] Quite apart from any practical application, studies of the reaction kinetics of metal clusters with small molecules have demonstrated dramatic cluster size dependence of reaction rate constants.[75] An understanding of the properties of metal oxides as a function of size, geometry, and reactivity is important if these materials are to be incorporated into polymers for sensor applications. The composites formed from these materials may be much different that the individual materials.

Growth of a crystal also coincides with advances in understanding intermolecular interactions and supramolecular chemistry.[76] Several aspects of solid-state chemistry are of increasing relevance to chemical sensors such as the application of cooperative binding to the differentiation of similar analytes.[77] Formation of metal oxide clusters with surface-adsorbed reactive organic groups has been achieved. Preparation of an interesting new type of inorganic–organic hybrid polymer with unique properties is also possible.[78] In summary, metal oxides provide both catalysts and catalytic supports that if used with ICPs may produce composite materials with unique sensing properties. However, the catalytic and reactive properties must be understood and exploited to develop selective chemical sensors which are targeted to specific analyte detection.

2.4. Phthalocyanines and Related Complexes

Pyrrole-based macrocycles such as metalloporphyrins have a similar structure to phthalocyanines (Pc). Porphyrins, which are less stable to degradation than phthalocyanines, have been used to mimic naturally occurring metal porphyrin complexes (e.g., cytochrome *c*, hemoglobin, and myoglobin). Specifically, metallophthalocyanines have been of interest for their high thermal stability and well-defined redox activity in sensing applications.[79] These compounds are organic p-type semiconductors formed from three distinct components: the macrocycle, the peripheral substituent, and the metal ion coordinated in the core of the molecule.[80] Each of these components contributes to the total selectivity of a sensing layer via manipulation of the metal center and substitution of functional groups on the organic ring.[81] Their ability to coordinate with almost all the metals and some nonmetals present in the Periodic Table results in a huge number of sensors that have been prepared using the same macrocycle. In solid-state gas sensors the conduction mechanism and molecular interaction contribute to the signal through either binding of the analyte to metal coordination sites or competition with O_2 for occupied metal surface sites. There is also a possibility of weak binding (physisorption) to the organic region of the phthalocyanine molecule for noncoordinating analytes, which may be governed by weak hydrophobic or charge-transfer interactions. The later interaction is related to formation of charge-transfer complexes through coordination of the target, O_2 (π-electron acceptor), to metallophthalocyanine (MPc) metal centers at the air/phthalocyanine interface. The interaction leads to formation of oxidized MPc^+ complex where the positive charge is delocalized over the phthalocyanine ring and reduces O_2^- species with injection of hole charge carriers into the bulk solid.[82] Resistive sensing concentrates mostly on p-type metallophthalocyanine thin films interacting with oxidizing gases, such as ozone and NO_x. The sensing mechanism is based on the gas interacting with the MPc, resulting in injection of holes and an increase in the current. Interaction of phthalocyanines with reducing gases, such as NH_3, has the opposite effect.[83] The advantage of these materials is that phthalocyanine films can be utilized for gas sensing at temperatures much lower than comparable metal oxide sensors.[84]

An alternative method for detection involves use of the materials as electrocatalysts. For example, detection of nitric oxide in biological systems on gold electrode and determination of nitrite in real samples using polymeric nickel tetraaminophthalocyanine (p-NiTAPc) film coated glassy carbon electrode has been achieved using the materials as electrocatalysts.[85] In addition, detection of NO in biological samples in the presence of interfering ions such as NO_2 and neurotransmitters has been achieved by immobilization of the porphyrin on the electrodes using thiolate coordination chemistry.[86] For good catalytic activity the catalyst must lower the oxidation and/or reduction potentials of the species. Therefore, an important factor in the catalytic activity of immobilized MPc complexes is identification of the oxidation or reduction site. MPc complexes with metal-based oxidation processes are expected to show better catalytic activity toward oxidation or reduction of analytes than ring-based processes. However, this fact has not been proven to be a general rule. It was found that in some cases the monomeric species of MPc are better catalysts than the aggregated complex. The catalytic activity depends on the thickness, conductivity, and method of immobilization of the film. In order to improve the selectivity of the sensor, Nafion has been included to help eliminate interference from other ions. However, Nafion tends to reduce the sensitivity of the sensor.

In summary, MPc should act as a good catalyst by enhancing sensitivity, be stable for prolonged use at different temperatures and pH values, and offer good selectivity for analyte over its oxidation products and other interfering species. One can therefore envision that incorporation of MPc into an ICP may optimize the sensing properties due to the nanostructure of the polymer. The improved nanostructured architecture of thin composite films may enhance interactions between the components and the conducting substrate and maximize diffusion of the guest molecules into the film.

2.5. Biologically Active Materials

The field of bioanalytical chemistry continues to expand encompassing biologically active materials, which utilize enzymes, proteins (amino acids), DNA, antibodies, and antigens. A large portion of the biosensors developed thus far have utilized enzymatic reactions. These systems use enzymes that are affixed, immobilized, or encapsulated in a variety of matrix materials. More recently more novel materials have been used, including carbon nanotubes,[87] gold particles,[88] proteins (amino acids),[89] and DNA,[90] to provide interaction sites for biological recognition components or analytes. The matrix must be chemically inert and not change the properties of the biological component so that the reactivity, potency, or interaction is not lost. In addition, the matrix must have open geometry so that the target analyte can access the biological component. Use of polymer matrices for biosensors has been reviewed previously.[91]

Detection of biologically active species is typically achieved using either optical or electrochemical methods. For electrochemical systems the biological transducer is incorporated in such a way that signal transduction results in a measurable current. Optical methods require that the biologically active component causes changes in the optical properties such as UV−vis absorbance and fluorescence intensity. In most cases this is achieved by incorporation of a biologically selective enzyme through electrostatic interactions or covalent bonding.[92] These systems have been reviewed previously and will not be extensively discussed in this review.[93]

Polymers are one common host matrix that are suitable for incorporation and trapping of enzymes.[94] Electropolymerization of nonconducting films like polyphenol, poly(1,2- diaminobenzene), poly(1,3-diaminobenzene), and poly(*o*-aminophenol) in the presence of an enzyme has been achieved with controlled enzyme loading. The enzymes remain active during polymerization and encapsulation because these films are generated from water-soluble monomers. Thin uniform films that filter electroactive interferents are possible, minimizing poisoning of the enzyme. Enzyme layers prepared by electropolymerization of *p*-aminophenol and glucose oxidase (GOx) have shown excellent characteristics in glucose sensor performance.[95]

Similarly, use of high-volume sol−gels[96] and zeolytes[97] as immobilization matrices has been realized. The large open volumes of sol−gels and zeolites provide attractive voids for incorporation of biologically active materials. In addition, the large open volumes allow rapid diffusion of analytes into the structure. Finally, two-dimensional arrays of self-assembled biologically active materials have been achieved, eliminating the need for secondary matrices. In these systems the biologically active component is typically covalently attached to the surface using well-known assembly chemistry such as the metal/thiolate interaction.[98]

3. Advances in Composites of Inherently Conducting Polymers

The general sensing mechanism is based on changes in the physical, chemical, or mechanical properties of the polymer when exposed to analyte. For example, when a conducting composite is exposed to a vapor it permeates into the polymer causing it to expand. The vapor-induced expansion of the polymer reduces the number of electrically conducting pathways for charge carriers. As a result, the electrical resistance of the composite rises. The high segment chain mobility of the ICP in the composite is an important requirement for good absorption of vapors or gases. This property can be improved through addition of nonconducting polymer, carbon, metal, or metal oxide particulates, or biological materials as they create amorphous, flexible regions around the ICP polymer chains in the composite. Consequently, they can be used to increase the number of interacting sites with the analyte, increase the intra- and interchain mobility of charge in ICP polymer chains or even change the affinity of the composite for the electron-donor or -acceptor gas. Furthermore, they can be used as a transducer matrix to convert the ionic charge into an electronic one, as a mediator and sometimes even as a catalyst. In the following section we will try to describe the role of the various components in the ICP composite materials with respect to sensitivity, response, and recovery time of the generated sensor signal that is a complex combination of transport properties within the host matrix and chemical interaction with the analyte.

For application of composites in sensor devices, two important factors need to be addressed: functionality and processability. These properties are related to the aspect ratio of the two components in the matrix, the interfacial adhesion between the additives, electrical conductivity, and structure. All of the properties are greatly influenced by the method used to obtain them, which essentially defines the fundamental challenge for applied ICP/CNT composite research. How does one effectively manipulate nanoscale building blocks to assemble useful nanoscale materials? Besides these essential factors, the properties of the composite can also be affected by the geometric structure of the material itself since it can be processed in the form of films, pellets, and wires. The differences in the volumetric factors between these structures cannot be neglected because they dramatically influence the diffusion of species into the composite and can affect the magnitude of the sensor response. More compact structures or thicker films may slow diffusion and be responsible for slow sensor response. On the other hand, thin films or fibers will be limited in the number of interacting sites, which may become the limiting factor for the dynamic range of the sensor response. Furthermore, processing parameters used for fabrication of structured composites affect, e.g., crystallinity and porosity in these materials.

Although the method of ICP/polymer composite sensors preparation is important, selection of the detection method for an analyte is equally important. For example, electronic properties that are strongly influenced by the preparation methods of ICP/polymer composites will have an impact on conductivity changes in conductive sensors. In contrast, in potentiometric sensors the measured change in anion or cation concentration in solution or in work function will depend strongly on the starting redox composition of the polymer.

3.1. Composites with Nonconducting Polymers

A useful approach to overcome some of the physical and chemical limitations, including the processability and mechanical and thermochemical stability of ICPs, involves combining these materials with other well-known nonconducting polymers, such as poly(vinylalcohol) (PVA), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinylacetate) (PVAc).[99] The resulting composite combines the advantageous electrical, redox, or optical properties of ICP with the mechanical properties of the host polymer through the ratio of ICP verses the insulating polymer.[100] The intrinsic conductivity of the ICP is not the key factor governing the electrical conductivity of the ICP/polymer composite films. Rather the processability of the two components in solution and the extent of dispersion of the conducting polymer inside the insulating polymer matrix are key.[101] In addition, the extent of dispersion of the ICP particles based on the solubility of the insulating matrix in the common solvent and the solvent's ability to swell and diminish heterogeneous domains inside the insulating polymer matrix strongly influences the electrical properties.

The solvent contributes to changes in the morphology of the film, which changes the response magnitude and reversibility of the sensor. Therefore, it is possible to vary sensitivity toward alcohols and amines and relative humidity by choosing the appropriate polymer matrix and solvent system for casting. However, it is not possible to modify the sensor's selectivity within the same polymer matrix. Higher solubility for the ICP in common solvent has been achieved using an anionic surfactant such as dodecyl benzenesulfonic acid (DBSA) that is also a dopant for the ICP precursor.

Chemical sensors based on coupling of the polymer swelling to optical and magneto- and electrochemical transduction technologies have been recently reviewed.[102] These composites have been categorized in terms of the production process as either homogeneous or heterogeneous systems. In homogeneous systems polymerization of ICP monomer is conducted in the presence of the nonconducting host of the polymeric matrix in solution. In heterogeneous systems polymerization is carried out via emulsion, colloidal dispersion of ICP particles, or thermal processing.[103] The thermally processed composites have percolation thresholds that are at least 1 order of magnitude higher than the lowest values obtained from solution-processed blends. Thermal processing methods provide poor structural control of the morphology. The solution and thermal processability of doped conjugated polymers allows production of conducting fibers with more open geometry. Properties of these composites such as degradation mechanism, electrochemical behavior in nonaqueous media, resistivity changes in relation to dispersion concentration, ion-exchange properties, conductivity, and photoconductivity studies have been examined previously.[104]

It can be concluded that the structure and mechanical properties of the electrically insulating polymer in the composite govern the sorption of the analyte molecule into the blend matrix and thus facilitate a change in the effective volume fraction of the conductive ICP phase. The ability of adjacent charge carriers in the ICP to hop or tunnel is controlled by potential barrier between the hopping sites and the host polymer, which can be manipulated by temperature.[105] In general, temperature-dependent sensor sensitivity to a particular gas is governed by the ratio of the two components in the composite and by the sensor–gas equilibria.

3.1.1. Composites with Hydrophilic Polymers

The solubility of various nonconducting polymers in water is well known and can be utilized to prepare ICP/polymer composites. However, water solubility implies that the materials will be sensitive to water vapor and that relative humidity must be monitored and evaluated before use as sensor materials. In some cases the sensitivity to water vapor can be used to produce highly reproducible humidity sensors. Various ICP polymers have been prepared in the presence of "water-soluble" polymers including PVA and PMMA, polymer (poly-*N*-vinyl pyrrolidin-2-one (PVP)), and ethylene vinyl acetate (EVA). Composites of polypyrrole with poly(vinyl acetate) with ∼27% PPy (PPy/PVAc) were cast as smooth, strong, and flexible films with electrical conductivity comparable to that of PPy and mechanical properties similar to those of the host polymer. The composite material demonstrates the importance of combining two materials and the benefit of mixing physical and chemical properties of the two dissimilar materials. The threshold conductivity for the composite was reached at 5% of PPy in the host matrix. The environmental stability of the PPy/polymer composite is improved relative to PPy films that can loose up to 50–65% of their conductivity after 45 days of exposure to the atmosphere.

PANI/PVA composites have also been prepared with variable amounts of PANI in the composite. Composites with more than 20% by weight of PANI in PVA are immiscible. However, when less than 10% of PANI is present, the composite is miscible. In general, processed PANI/PVA composite films (150 μm thick) do not show any change with respect to relative humidity between 10% and 60%. Also, PVA alone does not show significant impedance changes over the same relative humidity range. When the miscible PANI/PVA composite is exposed to relative humidity between 60% and 90%, the resistance decreases from the high MOhm range to lower values. The resistance of the immiscible PANI/PVA composite increases from the lower kOhm range to higher values for relative humidity between 60% and 90%.[106] It is important to note that a relatively small increase in the minority component PANI has a dramatic influence on the overall properties of the composite. The changes have been attributed to swelling of the PVA, which leads to separation of the conducting ICP/polymer domains for the composites. The overall resistance is based on competitive processes where the resistivity of PANI and PVA decreases and increases, respectively, at high humidity. PANI/PVP composites provide another example of composite materials with high sensitivity to relative humidity. These composites are prepared using poly-*N*-vinyl pyrrolidin-2-one (PVP), which has high affinity for the water vapor.[102] However, this film is less sensitive toward NH_3 than pure PANI. This discrepancy was attributed to the low affinity of the PVP for NH_3 sorption. In this example the properties of the PANI composite do not necessarily produce a better sensing material. Rather, it demonstrates the influence of each material in the composite on the overall sensing characteristics.

3.1.2. Composites with Hydrophobic Polymers

An attractive alternative to the PANI/PVA, water-soluble composite, is the PANI with styrene–butyl acrylate (SBA) copolymer films doped with weak acid.[107] The composite shows a linear resistive response for relative humidity between 20% and 95%, fast response time (4–5 s) measured in stepwise increments (of 10% relative humidity), and fast recovery times (10 s). The films were found to be stable for more than 1 year and at temperatures below 50 °C. Wallace et al. reported reliable and predictable linear responses with over a 100% resistance change over a 95% change in relative humidity for PANI and poly(butyl acrylate-co-vinyl acetate) (P(BuA-VAc)) copolymer (40% w/w). The composite with 15% w/w of PANI showed an exponential response with increased sensitivities with an 800% resistance change over a 95% change in relative humidity. The only disadvantage to PANI/P(BuA-VAc) composite is that the response showed a slow but consistent drift which was attributed to an overoxidation of PANI in air. However, the high sensitivity of the composite far outweighs the drift associated with decomposition.

Despite the use of relatively low hydrophilic matrix polymers such as poly(methylmethacrylate) or more hydrophobic polymers such as polystyrene, the influence of humidity on the ammonia response of PANI/PMMA and

PANI/PS sensor films was consistent with expected results. PANI doped with bis(2-ethyl hexyl) hydrogen phosphate (DiOHP) was mixed with poly(methyl methacrylate) (PMMA) and polystyrene (PS) and dissolved in toluene.[108] The resulting solution of polymers in toluene was cast to produce free-standing films. Use of toluene as casting solvent introduces porosity in the PANI-PS and PANI-PMMA blend favorable to high diffusion of gases into the membranes. Furthermore, PANI aggregates formed that were homogeneously distributed and completely covered by the host polymer in the matrix in the PANI/DiOHP/PS film. In contrast, PANI aggregates appear to form inside the porous matrix of the composite for PANI/DiOHP/PMMA composites. These aggregates introduce porosity into the PANI-PMMA blend and enhance the sensor response and reversibility. The composition of the protonated PANI in the PANI/DiOHP/PMMA and PANI/DiOHP/PS blends was 65.3%. The conductivity of the films decreased monotonously with increasing relative humidity from 15% to 85%. It is likely that the water molecules interact with the doped PANI, forming hydrogen bonds between the water molecules and the PANI backbone or the donor molecules, influencing the electronic properties of the composites. The PANI/DiOHP/PMMA composite showed larger decreases in conductivity than PANI/DiOHP/PS due to the higher porosity of PMMA host matrix. It was shown that the PANI/DiOHP/PS and PANI/DiOHP/PMMA blends have much better environmental stability than pure PANI films. In contrast to many of the composites discussed thus far, polypyrrole films chemically polymerized on poly(etheretherketone) (PEEK) and poly(methylmethacrylate) (PMMA) show high sensitivity to ammonia and amines at 100% RH with detection limits of 1 ppm. In addition, the composites can be used in biochemical applications because they are stable in aqueous environment.[109] Synthesis of 250 nm thick layer of PPy/PEEK composite has been achieved. In contrast, PPy/PMMA formed only a monolayer of ~50 nm spheres. The PPy polymerized on PEEK was more sensitive to ammonia and showed little sensitivity to ethanol or water in contrast to PPy deposited on PMMA or to a neat PPy. In addition, the PPy/PEEK composite was approximately three times more stable over time than PPy/PMMA. Composites of PMMA or PS processed with PPy doped with naphthalenesulfonate were also successfully used as acetone/toluene and acetone/acetic acid sensors.[110]

The gas-sensing properties of PANI/nylon-6 composite have been evaluated with respect to NH_3, CO, and C_3H_8 detection and quantitation. These studies have focused on the influence of the acid dopant on the sensing properties of the materials. The composites with monocarboxylic acid doped PANI including formic acid, acrylic acid, and dodecyl benzenesulfonic acid respond rapidly to NH_3 gas. In contrast, CO and C_3H_8 gases have no significant effect on changes in the electrical resistance of the composite or neat PANI material.[111]

It was also shown that pellets produced from PANI doped with HNO_3 or camphorsulfonic acid (CSA) have slightly higher electrical conductivity when compared to pellets of PANI/polyimide (PI) doped with either HNO_3 or CSI. The electrical conductivity values of PANI-HNO_3/PI and PANI-CSA/PI composites are comparable, in contrast to pellets made from homopolymer alone. The crystallinity of the PANI/PI composites doped with different acids is the key similar conductivity of the materials. Upon contact of the PANI-CSA in a form of a pristine material or composite with CO, known as oxidizing gas, an electron is transferred from the π-electron network of PANI to the gas, making the polymer positively charged. The charge carriers give rise to increased electrical conductivity of the film. The presence of polyimide in the PANI-CSA pellet improves the sensitivity toward CO interaction due to the fact that the conductivity is smaller by an order of magnitude when compared to the pristine polymer. On the other hand, the electrical conductivity responses are comparable.[112] Addition of polyimide to PANI not only reduces brittleness of the film but also improves electrical sensitivity toward CO by increasing the range of exposure temperatures accessible. On the basis of this observation it is expected that the temperature dependence may be used to improve selectivity of PANI/PI composites to gases or vapors by influencing the permeability or the displacement of water from the surface.

Generally, the gas sensitivity of the ICP/nonconducting polymers is considerably larger (1 or 2 order of magnitude) than that of the ICPs for the hydrophobic vapor analytes (xylene, benzene, acetone) at high vapor concentrations. Selective conductivity responses have been reported toward acetone and toluene or acetone and acetic acid for polypyrrole doped with naphthalene sulfonic acid (NS) using polystyrene (PS) or polymethacrylate (PMMA) as a nonconducting matrix.[113] The selectivity was attributed to solubility parameters of the nonconducting polymers that are comparable to acetone.[114] The selective conductivity response was controlled by temperature. It originated from two effects: the swelling of the nonconducting matrix that separated the conductive PPy particles and the PPy-NS interactions with the vapor itself. Moreover, the sensitivity to water was successfully eliminated. However, the long induction period and poorly reproducible responses remains a challenge in the use of these materials as sensors.

In summary, preparation of ICP/nonconducting polymer as a composite is simple. However, use of ICP/nonconducting polymers as sensitive, selective sensors can only be accomplished if the properties of the combined materials are adequately understood. For example, the ratio of the components in the matrix must be strictly controlled since it affects the reproducibility of the film sheet resistance and sensing device performance.

3.1.3. Multicomponent Composites

In ternary blend systems a conducting polymer is soluble in a uniform mixed nonconducting polymer matrix and does not interfere with the miscibility between the components of the nonconducting matrix. It has been reported that mixed matrices of copolyamide (CoPA)/ethylene vinyl acetate) (EVA) prepared with various PANI concentrations can be utilized as sensors for a homologous series of alcohols. The highest decrease in resistance correlated well with the polarity of the analytes.[115] The solubility difference of ICP in CoPA and EVA creates a continuous morphology for containing a highly conjugated path in the nonconjugated matrix. Therefore, the properties of the ternary polymer blend system are frequently better than conductive composites containing nonpolymeric conductive phases like carbon black or metal particles. The most prominent difference between these systems is that carbon black (CB) or metal particles do not produce as high an electronic conduction path in the matrix. Generally speaking, the higher electrical conductivity of the composite films provides higher signal-to-noise and reproducibility.

Favorable miscibility of ICP with the polymer components of the host matrix can easily be investigated using UV−vis, FTIR spectroscopy, optical microscopy, and differential scanning calorimetry. For example, the blue shift of the $\pi-\pi^*$ transition of ICP observed in the UV−vis spectrum signals the change in the conjugation length of the ICP and it splitting the miscibility with the polymer blend, vibrational shifts in the FTIR, and flattening of bands signals possible molecular interactions in the system, melting point depression, the miscibility and visual examination of the changes in the morphology of the material. In summary, the ternary type of polymer system offers expanded flexibility for realizing high-performance semiconducting architectures which can eliminate the need to design all of the performance requirements into the active semiconducting polymer. In general, sensors using these blends have low power consumption, operate at ambient temperature, and show reversible adsorption/desorption kinetics which are favorable in sensor applications.

3.2. Composites with Carbon Black and Carbon Nanotubes

Electrically conductive composites with carbon black (CB) or carbon nanotubes (CNT) and ICP have been produced and their advances in chemical sensing application reviewed.[116] These composites are obtained using two methods. The first method consists of the direct mixing of carbon black (CB), dispersion of CNT with or without ICP, or polymerization of ICP on the dried CNT networks. In the chemical or electrochemical oxidative polymerization of the ICP monomer CNTs act a supplementary reactive reagent. All the preparation methods lead to similar composites with improved electrical and mechanical properties of the ICP.

Carbon black particulates are one of the simplest carbon materials that have been particularly useful in the form of ICP/CB composite for the electrochemical detection of metal cations using stripping voltammetry.[117] The environmentally inert PANI/CB composite, prepared in porous glass as an electrode, showed high chemical and physical stability and allowed high reproducibility for the electrochemical accumulation and sensing of metal cations. These composite electrodes allow more hazardous Hg electrodes to be eliminated.

Addition of carbon structures using carbon nanotubes produces composites with enhanced properties relative to ICP/CB composites due primarily to the higher surface area. Most of the sensor applications of ICP/CNT composite have focused primarily on polyaniline, polypyrrole, polythiophene, and poly(3,4-ethylenedioxythiophene) (PEDOT) and characterization of their synergistic electronic and sensing properties. Different interface reactions between the ICP polymer and CNTs can be created which depend on the synthesis process. The interaction of aniline with CNT during polymerization can form charge-transfer complexes associated with disorder in the graphite lattice and defects on the carbon nanotubes. Alternatively, CNTs can create binding sites with the precursor ICP. The interaction between the dispersed ICP and carboxylated CNTs in a solvent can form covalent bonds that lead to polymer-functionalized CNTs and CNT doped polymer. In the case of chemical polymerization of ICP monomer in the presence of CNTs, the radical anion of the CNTs interacts with the positive charges on the ICP, resulting in polymer-functionalized CNTs.[118]

The electrical conductivity and structure of the composite is greatly influenced by the method used prepare the composite and the relative composition of CNT versus polymer. Preparation of the PANI/CNT composites from solutions of PANI (EB) in *N*,*N* -dimethyl propylene urea (DMPU) containing different amounts of the CNTs (1−5%)[119] have been compared with poly(3-hexylthiophene) (P3HT) with nonfunctionalized and functionalized solubilized SWCNTs in chloroform.[120] A rise in conductivity was observed only in the case of functionalized SWCNTs-P3HT composite having 1−5% weight content of nanotubes. In contrast, the nonfunctionalized SWCNTs-P3HT composite requires almost 20% by weight of nanotubes in the matrix to obtain the same level of conductivity as the functionalized SWCNTs. Although conductivity alone is not the dominant factor for ICP/CNT sensor applications it demonstrates the influence of carbon composition on the electronic properties of the composites. Since conductivity changes can be utilized as a detection method the functionalized composites may provide a more suitable starting material for development of chemical sensors. Finally, functionalization of the CNT surface not only leads to better dispersibility of the CNTs in various organic solvents[121] but also allows grafting of the ICP on to the wall of the nanotube, (CNT-*f*-ICP).[122] In addition, it increases the strength of the interface between the CNT and the ICP matrix and contributes to its environmental stability.

Fabrication of PANI/CNT composites through the electrostatic adsorption of the anilinium cation to MWNTs functionalized with COO^--functionalized MWNT requires only a very small amount of CNTs to form a conducting network chemiresistor.[123] The thickness of the films is an issue because the films are typically much thinner using this synthetic technique. Therefore, the thin film response is faster, but the overall analytical sensitivity is limited.[124] For thicker films chemisorption and physisorption can result in long recovery times. In fact, pure ICP does not show a high degree of chemisorption or physisorption in the absence of the MWNT. Operation of the conductometric sensor at higher temperature may enhance the desorption process of the chemisorbed gas and shorten the recovery time but can also decrease the overall sensor response.

The mechanism for the interaction of ICP/CNT composite with gas or vapor and the molecular selectivity have not yet been detailed. It has been suggested that it is based on charge-transfer interactions between the composite and the analyte. Furthermore, it has been also reported that cast membranes of chemically polymerized ICP/CNT material may yield more uniform coatings with much higher surface area than electrochemically polymerized material.[125] Multipulse chronoamperometric electropolymerization (MCE) has been used to fabricate composites with larger specific area, enhanced electronic conductivity, and ionic transport capacity critical for electroanalytical sensors.[126] In general, higher surface areas provide an increased number of interaction sites within the composite that are available for sensing.

The selective responses of chemoresistor to polar and nonpolar vapors can be predicted based on the ionization potential difference of the vapors. The greater the ionization potential, the weaker the polarization should be. This was demonstrated using a chemiresistor fabricated with a paste made from chemically polymerized 3-methylthiophene in the presence of COOH-functionalized MWCNTs, mixed with polyethylene oxide (used as a binder) deposited between two palladium electrodes. This chemiresistor was sensitive to chloromethanes (CH_2Cl_2, $CHCl_3$, CCl_4, CH_4) with fast response times. However, it was not sensitive to acetone, acetaldehyde, benzaldehyde, tetrahydrofuran, methanol, and ethanol vapors providing high selectivity.[127] The high selectivity of this composite was based on the analyte adsorptivities during analyte interaction. The suggested mechanism involves lowering of the free energy of the analyte due to the polarized structure of the composite, reducing electron flow in the sensor circuit. Similar interactions have been exploited using electron donors such of ammonia, trimethylamine, and triethylamine vapors with CNTs-COOH/PANI composites.[128] The changes in electron affinity associated with functional groups such as methyl, ethyl, and hydrogen leads to variation in gas sensitivity and response rate of the chemiresistor. It was shown that addition of CNT to PANI actually reduced the sensitivity to triethylamine, but the current baseline increased greatly which is favorable for the stability of the sensor. The existence of a strong interaction between CNT and PANI was shown to be an efficient way to adjust the baseline current and properties of gas sensors. In contrast, strong interactions between the analyte and the specific binding sites in the composite contribute to a high, irreversible response.

The effect of adsorption of gas molecules on functionalized field-effect-transistor have also been tested. However, the mechanism for the enhanced sensitivity has not been determined. The results are not fully understood and somewhat controversial due to possible modulation of Schotky barriers.[129] For example, two distinct responses were observed for the polyethyleneimine (PEI)/CNT-functionalized FET upon exposure to the electron-withdrawing NO_2 molecules. A steep and nonlinear conductance change at low gas concentration (up to 20 ppm) and linear conductance change at high gas concentration were observed. It has been suggested that the response at high concentrations may account for the charge transfer between the adsorbed gas molecules and the CNT/composite. A Langmuir-type isotherm can be used to describe adsorption at low concentrations of NO_2 consistent with a steep and nonlinear change in conductivity. This observation was independent of the type of the coating (CNT with PEI or without), suggesting that the PEI does not alter the binding energy of adsorbed molecules. The response at high concentration has to be taken into account when the vapor is at ppt concentration.[130]

Recent studies have also demonstrated that CNTs enhance the electrocatalytic properties of phosphomolybdic acid ($H_3PMo_{12}O_{40}$) in polypyrrole films when used as an amperometric sensor. The studies are predicated on the enhanced catalytic activity associated with the high electron density of the polymer and surface reactivity of the composite. Use of galvanostatically deposited film of PPy doped with the heteropolyanion on CNT-modified gold electrode has been particularly useful in the detection and quantitation of nitrite.[131] An enhanced electrocatalytic reduction current for nitrite was observed for PPy-($H_3PMo_{12}O_{40}$)/CNT/Au as compared to the electrode without CNT. The reduced response of PPy-($H_3PMo_{12}O_{40}$)/Au demonstrated that CNTs promote electron transfer between the heteropolyanion and the electrode surface. The amperometric response to nitrite was about four times higher than that of the electrode without CNT reaching a detection limit of 1×10^{-6} M. A similar method for grafting electrochemically deposited PANI films on CNT and incorporation of nanoclusters of nickel hexacyanoferrates has been applied for detection of cesium ions.[132]

New electroanalytical applications have also been examined with ICP/CNT composites. The oxidation state of the ICP is particularly relevant to these applications. Specifically the equilibrium potential of the two partially oxidized redox couples of the ICPs are critical. In polyaniline the equilibrium potential is defined by the ratio of the deprotonated base (emeraldine base, EB) and the protonated salt (emeraldine salt, ES).[133] Composites of PANI/CNT networks (150−200 nm thick) deposited from sodium dodecylsulfate (SDS) and coated electrochemically with PPy or PANI showed reproducible, linear, fast, and stable pH responses in buffer solution of pH 1−13.[134] The dynamic range and stability of the response was significantly improved due to the higher thickness of the film and different types of binding sites present in the film when compared to pure CNT network. In addition, excellent electrocatalytic properties have been reported for overoxidized PPy/SWNT composite deposited on glassy carbon electrode (GCE) from sodium dodecyl sulfate. The oxidized composite has been used for amperometric sensing of nitrite, ascorbic acid, dopamine, and uric acid.[135] The useful concentration ranges for dopamine, uric acid, and ascorbic acid were between 1.0×10^{-3} and 1.0×10^{-6} M with detection limits of 3.8×10^{-7}, 7.4×10^{-7}, and 4.6×10^{-6}, respectively. The electrodes were stable, selective, and sensitive to the biological species.

The field of biosensing has also benefited from ICP/carbon composite materials. For example, amperometric glucose sensors have been made by modifying the platinum surface with CNTs followed by electrochemical deposition of 3,3′-diaminobenzidine (DAB). The DAB film introduces NH_2 functional groups into the composite that are use to immobilize glucose oxidase.[136] Although there are numerous glucose biosensors discussed in the literature, this material is more selective and has a higher response to glucose at a much lower potential than other materials. The lower detection potential allows suppressed interference signals from ascorbic acid or uric acid. The enhanced properties are the direct result of the symbiotic properties of the composite.

Preparation of poly(1,2-diaminobenzene)/CNTs nanoporous composite on a glassy carbon electrode via a multipulse chronoamperometric electropolymerization process has been demonstrated. The composite provides an excellent platform for fast determination (5 s) of NADH at a lower concentration range (from 2.0 μM to 4 mM) with detection limits of 0.5 μM in phosphate buffer. These values are significantly lower than the response of the polymer alone. That performance is a direct result of the enhanced electronic structure of the composite and high surface area afforded by the CNTs coated with polymer.[126]

ICP/carbon composites have been applied to a number of common biosensor systems. For example, an effective molecular template for the electrostatic rejection of dopamine has been prepared from a DNA-dispersed CNT in self-doped poly(anilineboronic acid). The sensor has improved conductivity, redox activity, and stability of the polymer in neutral solutions during dopamine detection at very low concentration (1 nM).[137] Similarly, electrochemical DNA biosensors based on nucleic acid recognition processes exploit the properties of ICP/CNT composites. For this system, PPy/MWCNTs-COOH-modified glassy carbon electrodes are incubated in the presence of 1-ethyl-3(3-dimethylaminopropyl) carbodiimide (EDAC), and NH_2-terminated ssDNA probes were used as the DNA hybridization transducer.[138] Finally, ICP/CNT composites have been used to detect complementary DNA sequences as low as 5.0×10^{-12} mol/L using electrochemical impedance without a hybridization marker or intercalator. Use of hybridized DNA probes provides a high degree of selectivity at a high cost. Therefore, when possible nonhybridized systems are preferred provided they are selective and sensitive for the target DNA structure.

In summary, it can be said that ICP/CNT composites are very useful for facilitating electron transfer and increasing efficiency of binding sites for specific sensing interactions without the need of redox mediators. However, they require functionalization because the carbon structures alone do not provide selective interfaces within the sensor composite. In addition, difficulties in incorporation of the carbon species must be overcome for proper accommodation within the sensor device structure. Provided these issues are addressed, the enhanced electronic conductivity of the carbon materials is promising to provide high sensitivity responses to a variety of analytes.

3.3. Composites with Metallic or Metal-Containing Components

Incorporation of metals, metal oxides, and organometallic species such as metallocenes in intrinsically conductive polymers can enhance electron transfer through a direct or mediated mechanism with improved conductivity and enhanced stability.[139] For these systems the electron-rich polymer often acts as a chemical receptor or scaffold for the secondary component. The electron density of the conductive polymer is important, providing stability to species that may be electron deficient. However, it has also been suggested that the polymer provides stability through exclusion of surface contaminants that may interfere with the surface chemistry of the deposit. The structure of the conductive polymer plays a role in the dispersion of the species, their aggregation, and formation of the composite material. The polymer is used to provide high surface, protection against the fouling of the metal catalyst, and a scaffold for high dispersion and anchoring of the metal particles. The conductivity of the composite allows the electron density of the polymer to be controlled through the applied thermodynamic potential which influences chemical reactions at the metal surface. The ability to finely disperse the secondary species in the polymer ensures high surface area and possible enhancement of the unique characteristics of the composite. The synthetic method employed is an important factor to consider with regard to the homogeneous distribution of the secondary component.

There are multiple methods used to prepare the ICP composite materials with metallic species distributed at the polymer surface in the vicinity of the electrode/polymer interface or throughout the bulk of the polymer. The approach used to introduce the metallic species typically determines the degree of dispersion or deposition. For example, dispersion of the polymer using pulsed deposition and relaxation (spontaneous reduction of the species) or co-deposition of the ICP with the active species using cyclic voltammetry has been utilized to introduce metal species.[140] One common approach involves the chemical reaction and uptake of a species by the conductive polymer. In this case the species are introduced by controlled reduction of metallic anions such as $AuCl_4^-$, $PtCl_4^{2-}$, and $PtCl_6^{2-}$ by manipulating the redox sites within the ICP.[141] The uptake of the negatively charged anion of interest is based on the oxidation of the polymer and the need to maintain charge neutrality in the system. Reduction of the anion occurs as the potential is switched to negative values. In contrast, the oxidized form of the metal species can be introduced to the polymer using metal salts followed by the electrochemical, chemical, or spontaneous reduction of the metallic species. The most common metals incorporated into the ICP include gold, platinum, and palladium as nano- or/and microparticles.

In many cases formation of the metal nanoparticles occurs prior to incorporation into conductive polymer matrix. In such cases, the preformed clusters of metal, metal oxides, or metallocenes are dispersed in solution containing the ICP precursor. Chemical oxidation of the precursor results in encapsulation of the metal species to form the ICP composite.[142] The resulting materials can then be cast onto substrates for subsequent applications. Recently, the direct chemical synthesis of composite materials using polymer precursors and oxidizing anions such as $AuCl_4^-$ and $PtCl_6^{2-}$ has been reported.[143] Each of the methods discussed has its advantages and disadvantages that must be weighed before they are used to prepare composite materials.

The properties and application of composite materials containing metals, metal oxides, and metallocenes are quite diverse. For example, polyaniline, polythiophene, and polypyrrole have all been utilized as scaffolds for the incorporation of metal species in catalytic applications.[144] Catalysis at metal surfaces embedded in conducting polymers is enhanced due to the conductive environment. The electrooxidation of CO adsorbed on Pt particles incorporated into the PANI film surface occurs at a lower positive potential than on bulk Pt alone. The oxidation potential depends not only on the thickness of PANI film but also on the amount of Pt particles incorporated into the PANI matrix.[145] Likewise, metal oxides such as SnO_2 and TiO_2 have received much attention due to their unique properties and use in applications such as fuel cells and batteries.[146] Metallocenes can be used for a host of applications based on their optical and electronic properties.[147] When combined with ICPs each of these materials provides unique properties that are consistent with the physical and chemical properties of the species.

The properties of the composite materials are exploited when developing chemical sensing applications. It is well known that nanoparticles demonstrate special size- and shape-dependent properties.[148] For example, the nanoparticle size and shape have significant effects on the localized surface plasmon resonance spectrum of Ag and Au nanoparticles.[149] The sensing application typically dictates the critical size of the metal species in the composite. It has been observed that aggregation and size distribution of the metal nanoparticles vary with the reaction time. It is difficult to control both the size distribution and aggregation of the metal particles embedded in the polymer matrix regardless of the technique used to create the composite. Therefore, the size of the metal particle is often inhomogeneous or variable. Within this section we would like to review some approaches for the synthesis and use of ICP/metallic species composites for chemical sensing.

3.3.1. Gold

Chemical sensors based on gold nanostructured particles are of interest for sensing gases and vapors and as binding sites for enzymes, proteins, and nucleotides. While the size of the gold cluster used to affix bioactive species is not critical, detection of gases at gold surfaces is dependent on this parameter. Therefore, the size distribution of gold in ICPs must be monitored based on the application. The dependence is governed by the shift of the binding energy of Au clusters in the PANI matrix associated with the cluster size. The binding energy of the smallest Au particle size (0.2 nm) has been determined to be 84.49 eV. In contrast, the binding energy for the largest (30 nm) Au particle is 84.09 eV, a difference of 0.40 eV. The properties of gold clusters, ∼5 nm, approaches bulk metal with respect to binding energies. In contrast, clusters of 1−2 nm diameter have approximately 30−250 atoms with higher binding energies.[150] In addition, the nanoscopic gold catalysts are active at much lower temperatures in comparison to platinum-group catalysts for CO oxidation.[151] There is a debate regarding the underlying basis for the activity of these nanoscale materials contributing to the complexity of Au-based catalysts.

The optical properties of nanoscale metal particles and composites are often unique. For example, femtosecond transient absorption dynamics of the gold and gold−polypyrrole nanoparticles by photoexcitation at wavelengths of 580 and 400 nm are different.[152] In contrast to gold nanoparticles, PPy/Au nanoparticles exhibit negligible changes in the time constants for electron−phonon interactions for increasing beam intensity. In addition, the amplitudes for phonon−phonon interactions of the gold polypyrrole nanoparticles are enhanced significantly with increasing beam intensity in comparison to bare gold nanoparticles. These features illustrate that polypyrrole provides an efficient channel for thermal energy relaxation of the gold nanoparticles in the PPy/Au composite. Not all optical properties are enhanced by formation of the PPy/Au composite. Photoexcitation of gold particles and the PPy/Au composite at 400 nm is nearly the same regardless of changes in the excitation intensity.

Chemical oxidation−reduction reactions that result in the uptake of gold into the conducting polymer can also be spontaneous. When the reaction conditions become thermodynamically unfavorable the process ceases. It was demonstrated that the spontaneous reduction of Au from halogenaurate salt in acidic solution into previously formed PANI films containing either HBF_4 or CH_3COOH acid dopant changes the work function of the PANI/Au composite. It needs to be pointed out that the nucleation and growth of the gold particles in the PANI is a continuous interplay between nucleation and diffusion of the aurate ions in the solution. The film morphology depends on the thickness and acid used for its polymerization, which affect the availability of nucleation sites (imine to amine ratio). The size of the Au clusters and their distribution within the polymer matrix is a function of the immersion time in solution.[153]

More recent studies have used the aniline monomer and metal anion, $AuCl_4^-$, to produce PANI/Au composites.[154] The one-step process has also been used to form PANI/Au structures in the presence of soft templates such as D-camphor-10-sulfonic acid (CSA), which acts as both a dopant and a surfactant in formation of one-dimensional PANI/Au coaxial nanocables with an average diameter of 50−60 nm and lengths of more than 1−2 μm.[155] It was found that the probability of formation and the size of the PANI/Au nanofiber depends on the molar ratio of aniline to $HAuCl_4$ and the concentration of CSA, respectively. The conductivity of a single gold/polyaniline nanocable was high, 77.2 S cm^{-1}. Hollow PANI nanotubes, with an average diameter of 50−60 nm, were also obtained successfully by dissolving the Au from the composite.

In contrast to the chemical synthesis of PANI/Au composite the thermodynamics of the synthesis can be controlled electrochemically with the applied electrochemical potential. In these processes the potential dependent uptake and reduction of $AuCl_4^-$ ions is achieved in the preformed polymer film of either PANI or PPy.[156] In addition, studies of the uptake of HCl in PANI films have identified a similar method for creating PANI/Au composites termed “moving electrochemical front” synthesis. The technique is based on the potential-dependent generation of chloroaurate ion at the sacrificial Au electrode surfaces during normal acid doping of the polymer. The electrochemical generation of $AuCl_4^-$ was reduced in the PANI film to form the PANI/Au composite.[148] Comparative experiments between the electrochemical and chemical method for Au formation in the PANI matrix have identified the synthetic differences between the composites.[139] In the case of electrochemically prepared PANI/Au composites the reduction of Au has been shown to reduce proton doping at the nitrogen heteroatom. Acid doping for the chemically prepared PANI/Au composite is relatively unchanged in comparison. The results indicate that electrochemically reduced gold nanoparticles interact more strongly with the polymer when they are formed electrochemically.

A unique approach for fabrication of H-bonded multilayer thin films with gold nanoparticles has been reported.[157] This system is unique because the composite is produced without the use of an additional reducing agent. The system reveals interesting nanostructural and spectroscopic properties that require further investigation. The impact of the synthetic method remains to be determined.

The number of sensors that utilize ICP/Au composite materials is quite small. However, the optical and catalytic properties of the composites are well studied and suggest that the materials can be utilized for chemical sensing. For example, conductive polymer/gold composite materials have been used in the amperometric sensing of NO_2. The analytical sensitivity of PANI/Au/Nafion composite is on the order of 2.54−1.40 mA/ppm for NO_2. The material does not specifically utilize gold clusters embedded in the polymer matrix. Rather, the gold is deposited on Nafion and the polyaniline is electrochemically grown on the Nafion/Au substrate to create the Nafion/Au/PANI sandwich structure. The membrane is then used to monitor the cathodic reduction of NO_2. The conductive polymer is an important component that improves the properties of the composite material. The Nafion/Au/PANI coating increases the sensitivity of the sensor relative to Au/Nafion alone.[158]

Aqueous-based ion sensing has been achieved using stripping analysis at gold surfaces. The motivation was primarily based on eliminating the need for mercury working electrodes in stripping analysis. Gold-modified carbon paint screen-printed electrodes were developed as an alternative to mercury-based electrodes for determination of metals such as lead, copper, and mercury.[159] More recently, conductive polymers have been utilized as a template for gold stripping electrode and detection of arsenic.[160] The composite material is prepared through the electrochemical reduction of gold in a PANI membrane formed on a glassy carbon electrode. For comparison, additional electrodes were prepared in the same manner on a pristine glassy carbon electrode without a thin layer of PANI. The work demonstrates that PANI provides a much higher surface area than glassy carbon alone that translates into higher sensitivity of the analytical device. The limit of detection for the sensor was calculated to be 0.4 ppb, well below concentrations that are considered safe.

More extensive work exists with respect to the application of conductive polymer/gold composite materials as biosensors. In many cases the gold is chemically modified to impart unique chemical characteristics that can be utilized for sensing. For example, use of gold and silver nanoparticles for glucose sensing has been recently reviewed.[161] This work utilized dextran rather than conductive polymers to prevent nanoparticles in solution from aggregating. Physical changes in the aggregation of gold particles in the presence of glucose were examined using the fluorescence activity of the gold at 650 nm. Use of conducting polymer/gold nanoparticles for glucose sensing has been achieved using the absorbance of the gold nanoparticles in the presence of glucose. The absorbance spectrum of polyaniline boronic acid/gold nanoparticle composite is extremely sensitive to the dielectric environment and shows a decrease in intensity of the band located at 543 nm as glucose concentration increases. The key to these sensors is the dispersion of nanoscopic gold into the polymer. In addition to the high surface area provided by the dispersion of nanoparticles of gold, the chemical properties of the nanodeposits are different from the bulk metal.[162] These two works were preliminary studies and did not provide any information regarding the selectivity or sensitivity of the composite systems with respect to the target analyte, glucose. These studies are examples of how ICP/Au nanoparticle composites can be utilized as glucose sensing materials. They also provide insight in the preparation and incorporation of the materials in electrochemical systems.

A more thorough study of glucose biosensing using conductive polymer/gold nanoparticle composites has been conducted.[163] In this study polyaniline/gold nanocomposites were produced in two steps. First, the $HAuCl_4$ was reacted with H_2O_2 to produce the nanoparticles of gold. This solution was then reacted with aniline to produce the composite material, PANI/Au. Electrodes were prepared by casting PANI/Au composite onto an electrode's surface, reacted with glucose oxidase, and capped with Nafion. Detection utilizes the H_2O_2 produced by the PANI/Au/enzyme/Nafion when glucose reacts with glucose oxidase. The sensor produced has a dynamic range between 1.0×10^{-6} and 8.0×10^{-4} mol/L and a detection limit of 5.0×10^{-7} mol/L. The amperometric sensitivity was calculated to be 2.3 mA/M.

The influence of structured composites on glucose sensing has also been examined. PANI/polystyrene/Au nanoparticle rods were prepared on electrode surfaces with glucose oxidase incorporated into the membrane.[164] Oxidation of glucose was examined for membranes with and without Au nanoparticles, and calibration plots were obtained for both. The membranes with Au were shown to be approximately two times more sensitive than membranes without the metal species. In addition, the structured rod membranes were 25 times more sensitive than simple membranes of the composite for equal gram weights of material used. The increase is attributed to higher surface area and a more open geometry for the rod membranes. Although there are few examples of PANI/Au composite biological sensors, the glucose studies suggest that other biosensing systems can be produced using similar enzymatic processes.

Plasma resonance sensors are quite common and have been used for a variety of surface-based sensing. In these sensors the gold nanoparticles are modified with secondary components such as antibodies, antigens, and self-assembled monolayers (SAMs) that act as signal transducers.[165] Interactions at the modified surface influence the localized surface plasmon resonance of the modified gold particles through changes in UV−vis absorption. The secondary components attached to the gold provide a selective interface for the target analyte to interact.[166] The high molar absorptivity associated with surface plasmon resonance ensures high analytical sensitivity for the devices.[167] A recent article has suggested that electroactive plasmonic sensors constructed from conductive polymer/metal composites may become a reality.[168] In this work, gold nanoparticles are sandwiched between PANI membranes and potential-dependent modulation of the surface plasmon resonance of the gold is observed. Reduction of the surface plasmon resonance is observed as PANI becomes more oxidized. This work suggested that the oxidation state of PANI might be utilized in sensing regimes based on surface plasmon resonance of the gold nanoparticles. The sensing mechanism highlights a symbiosis that exists between the polymer matrix and the gold particles being exploited in chemical sensing.

In addition, modification of gold nanocomposites can also be employed, opening other sensing pathways based on the immunoassay work discussed previously. Modification of gold surfaces is well known.[169] Monolayers of *n*-alkanethiol and functionalized alkanethiols have been self-assembled onto a gold surface, providing stable metal/organic surfaces that permit introduction of a variety of functional groups onto surfaces.[170] However, use of alkanethiol derivatives in conductive polymer/gold composites has not been thoroughly explored. One explanation could be their poor oxidative stability. The recently synthesized poly(propylenesulfide)-based copolymers that chemisorbed on gold surfaces and is much more robust to oxidation as compared to alkanethiolates may lead to a novel approach for surface modification.[171] Aside from that, a similar approach using thiol moieties seems logical to be transferred to conductive polymer/gold composites for gas-based sensing. The large surface area of the polymer and high dispersion of gold in the matrix should provide enhanced signal for sensor devices through the increase in surface area. More importantly, use of derivatized thiols imparts chemical selectivity to an otherwise nonselective surface. A recent review of self-assembled monolayers provides examples of thiol surfaces that have been utilized to develop selective sensors.[172]

3.3.2. Platinum and Palladium Metal

Inherently conducting polymer/platinum or palladium composites can be formed in much the same manner as the conductive ICP/gold composite materials discussed previously. The most common method to prepare PANI/Pt composites involves direct reduction of anions such as $PtCl_4^{2-}$ and $PtCl_6^{2-}$ into the polymer[173] or chemical synthesis of PANI in the presence of $PtCl_4^{2-}$ and $PtCl_6^{2-}$.[141] Similarly, synthesis of Nafion-PANI-Pd or Nafion-PANI-Pd composites on a Nafion-modified glassy carbon electrode has been accomplished.[174] Synthesis of ICP−metal nanoparticle composite materials having a nanofiber-like morphology has been carried out by Mallick et al.[175] The nanofibers composite was synthesized using 3,5-dimethyl aniline as a polymer precursor and Pd−acetate. During the reaction 3,5-dimethyl aniline undergoes oxidation and forms poly(3,5-dimethyl aniline), whereas reduction of Pd−acetate results in formation of Pd nanoparticles. The major advantage of this procedure is that both the polymer and the nanosized metal particulates are formed simultaneously yielding a good internal electrical contact between them. The dispersed Pd nanoparticulates were all of the same size (~2 nm). Polyaniline−Pd nanoparticle composite was also prepared by mixing previously formed polymer with Pd nanoparticles (Pd-NPs). Oyama et al. reported that the amount of Pd-NPs dispersed within the PANI film affects it redox chemistry.[176] The Pd-NPs are stable as metallic state Pd(0) in the PANI−Pd composite film, whereas it exists as ionic state Pd(II) by electrochemical reaction with PANI.

Conductive polymer/Pt and conductive polymer/Pd composites have been primarily utilized in fuel cell applications and catalysis. The catalytic oxidation reactions of formic acid, methanol, ethanol, and hydrazine at platinum composites have been evaluated for fuel cell applications.[177] Polyaniline/Nafion membranes with Pd have been used to examine the electrocatalytic oxidation of formic acid for fuel cell applications.[178] Other studies have examined the catalytic hydrogenation and oxidative coupling reactions at PANI/Pd composite materials.[179]

Use of conductive polymer/Pt and Pd composites for chemical sensing has been limited in comparison to development of materials for catalysis. However, there are a few studies that have identified sensing regimes that can utilize conductive/Pt and Pd composites. For example, amperometric sensing of hydrogen has been achieved at Nafion membranes containing platinum.[180] In this study the influence of Pt loading was examined with respect to the analytical sensitivity of the device. The results indicated that the highest sensitivity was on the order of 0.716 μA/ppm in the concentration range of 1260−5250 ppm. Finally, hydrogen sensing using Nafion/Pt composites has been examined.[181] The selectivity and sensitivity of the conductive polymer/Pt composite was maximized while minimizing Pt loading in this study. The hydrogen sensor produced using the Nafion/Pt composite had long-term stability at room temperature with an analytical sensitivity of 0.01 μA cm^{-2} ppm^{-1}.

Fewer examples of conductive polymer/Pd sensors exist in the literature. The chemical sensing of methanol using PANI/Pd nanocomposites has been achieved.[182] The material is produced through oxidative polymerization of aniline in the presence of Pd nanoparticles. The resistance of the composite was examined as a function of methanol vapor concentration over a concentration range of 1−2000 ppm. However, saturation of the sensor was observed at concentrations higher than 10 ppm, indicating that sensor has a very small dynamic range. The response of mixtures of other alcohols with methanol did not change the response of the sensor appreciably, indicating the composite selectivity responds to methanol in the presence of possible interfering species. Finally, palladium-modified multiwalled nanotubes have been utilized in the chemical sensing of benzene at room temperature.[183]

Although there are few examples of conductive polymer/Pd composite sensors in the literature, there are many examples of the use of Pd with other materials to produce sensors. Use of polystyrene/Pd nanocomposite for hydrogen sensing has been achieved.[184] Electrochemical detection of hydrazine has been achieved using multiwalled nanotubes “decorated” with Pd nanoparticles.[185] These works suggest that ICP/Pd composites may be utilized for similar sensing applications that build on the principals developed previously in the study of nonconducting polymer and CNT composites.

Biosensing applications have utilized the catalytic properties of the metal component of the ICP/Pt composites. Highly dispersed Pt particles in superfine-fibrous polyaniline (PANI) synthesized on stainless steel electrode have excellent electrocatalytic activity for H_2O_2 oxidation. When glucose oxidase is combined with the PANI/Pt composite the material functions as a glucose sensor. Detection of hydrogen peroxide generated in the presence of glucose oxidase is utilized to detect the sugar.[186] The enzyme electrode has excellent performance with a large steady-state current response. In addition, the amperometric response time to glucose is fast with minimal interference from other biological components encountered including uric and ascorbic acid. It was observed that with addition of Pt the interference from uric and ascorbic acid was greatly diminished and minimized.

In summary, ICPs can be utilized for dispersion of metal species in place of other materials to produce composites with similar or new sensing properties. Specifically, catalytic reactions and sensing regimes that utilize Pd and Pt particles and conductive polymers should be examined more thoroughly. When possible, sensing applications that utilize nonconductive/metal composites should be reevaluated with ICPs. The advantages of high electron density and potential-dependent control of the oxidation state of the conductive polymer should be utilized and when possible evaluated with respect to known sensing mechanisms.

3.3.3. Copper and Nickel Metal

Although Au, Pt, and Pd are the most common metallic species that have been used to produce ICP/metal composites, Cu and Ni have also received some attention. Use of PANI/Cu for detection of chloroform vapor at ppm levels has been tested.[187] The composite was prepared by adding copper colloid during chemical polymerization of aniline. It was used as a pressed pellet for sensing applications where the composite functioned as a chemoresistor. On the basis of FTIR spectra and a comparative study of a neat PANI it was concluded that the unique surface activity of Cu nanoparticles plays a major role in the reproducible and reversible response of the composite to chloroform vapor.

Free-standing PANI/Ni film with a Ni content as high as 4.12% was prepared by a simple one-step electrochemical method.[188] It was shown that the size and distribution of the Ni deposits are influenced by the electrolytic bath composition and potential sweep rate. In addition, the PANI matrix exhibited excellent ferromagnetism after incorporation of Ni. It was determined that the electrical conductance of PANI was also modified by the presence of Ni in the polymer matrix.[189] For example, the conductivity of the composite was lower than that of neat PANI. The decrease in conductivity was attributed to the partial blockage of the conductive path by the Ni particles embedded in the polymer matrix. The synthesis of PANI/Ni/PANI composite materials has also been achieved using layer-by-layer deposition.[190] The composite was characterized electrochemically. It was shown that the nickel−nanoclusters induce changes in the structural morphology of PANI matrix, influencing the electrooxidation of PANI chains. In addition, the clusters cause bridging between the PANI chains/fibrils, promoting delocalization of electrons within the polymer.

A more novel application can be envisioned that utilizes the electrocatalytic activity of Ni/PANI and NiMo/PANI layers.[191] The materials show promise as catalytic materials for chemical and biological sensors. In addition, alloying nickel with transition metals (W, Mo, Fe) should increase the intrinsic electrocatalytic activity. Furthermore, the magnetic alloys can act as functional components for the separation of biorecognition complexes and amplified electrochemical sensing of DNA or antigen/antibody complexes. Preliminary studies on sensing properties of nickel incorporated into a Nafion have been conducted.[192] Potential-dependent switching of a magnetic responsive composite of 2.5 μM Nafion with 300 nm Ni particles obtained through a standard ion-exchange method as a function of applied current has been observed. Within a proper operational range of ±0.7 V, Ni-doped multifield responsive, ionic polymer−metal composite shows good paramagnetic characteristics and excellent electric responsive properties without oxidation-induced performance degradation.

3.3.4. Metal Oxides

Composites containing conductive polymers with metal oxides, TiO_2, ZrO_2, and WO_3 to name a few, have been produced. These composites minimize the need to operate at high temperature (300−500 °C), typical of bulk metal oxides. Composite sensors produced using ICP/metal oxides have enhanced stability and respond to both oxidizing (NO_2) and reducing gases (CO_2, CO, H_2). It is documented that the method of preparation of TiO_2 or SiO_2 influences the operating temperature. More recently it has been shown that sensors prepared from sol−gel microstructures of TiO_2 and SiO_2 can be operated at temperatures as low as 200 °C with high stability in the presence of CO and NO_2 gas.[193] TiO_2 and SiO_2 have been added to solutions containing aniline monomer and the chemical oxidant ammonium persulfate to form the sol−gel composite.[194] These materials show very high thermal stability with 75% retention of mass at temperatures in excess of 800 °C. Although these materials were not used as chemical sensors, the study demonstrates the high stability of these materials.

Use of ICP/TiO_2, SiO_2 nanocomposites for CO gas sensing has been examined, but the study is not detailed and does not provide either the dynamic concentration range for CO gas or the analytical sensitivity of the device prepared from the composite.[195] In addition, there is no attempt to examine possible interference from other gases. However, the study does demonstrate the response of the composite material to CO gas at room temperature. This study is important because it demonstrated that elevated temperatures are not required to observed changes in conductivity/resistance of the PANI/TiO_2, SiO_2 composite. It suggests that the ICP and nanostructure of the TiO_2 and SiO_2 deposits are important for lowering the operating temperatures of gas sensors when compared to bulk films.

Polypyrrole-, polyaniline-, or polyhexylthiophene-coated SnO_2 or TiO_2 nanoparticles were also prepared using the self-assembly (SLB) procedure.[196] The process was repeated multiple times to obtain the desired thickness of the nanocomposite films. The ultrathin films were used for CO, aromatic hydrocarbon, and NO_2 sensing applications. The change in resistance at room temperature upon exposure to NO_2 was recorded, decreasing exponentially with concentration. The results suggest that the gas may act as a dopant for the conducting polymer. The material demonstrated high sensitivity with large changes in resistance at all concentrations. It is worth noting that the response showed thickness dependence with instantaneous and highly reproducible response as the film thickness decreased. In addition, the thin films are better for low gas (ppb) detection levels. The composites demonstrated higher sensitivity, stability, and reversibility when compared to neat ICP films. In addition, elevated operating temperatures were not required, with polyhexylthiophene/SnO_2 nanocomposite films exhibiting good detection characteristics at room temperature. Additional studies of metal oxides doped with platinum and palladium have been examined. For example, surface-doped tin nanoparticles show a large increase of sensitivity in humid air and a surprising inversion of sensitivity toward carbon monoxide in dry atmosphere (relative humidity $\approx$ 5%) when going from undoped to Pd- or Pt-doped sensors.[197]

These studies are preliminary in nature and demonstrate the influence of metal doping on metal oxides. The impact of these systems remains to be evaluated. In contrast, the ICP/SnO_2 or TiO_2 composite systems have been shown to be one of the most interesting nanostructured materials for gas-sensing application. These materials show an excellent change in conductivity at room temperature and possess excellent optical and catalytic properties that can be utilized to develop chemical sensors.

3.3.5. Metal Phthalocyanines and Porphyrins

The composite materials produced from ICP and phthalocyanines demonstrate high electrical conductivity consistent with the properties of the polymer. For example, polyaniline/phthalocyanine (PANI/Pc) and polypyrrole/phthalocyanine (PPy/Pc) films have been prepared electrochemically on platinum electrodes from aqueous solutions containing pyrrole or aniline and a salt of the oligomeric nickel or cobalt phthalocyanine.[198] Incorporation of large anions based on oligomeric metal/phthalocyanines and polypyrrole or polyaniline favors cation insertion during their normal redox process. In contrast to PPy/NiPPc or PPy/CoPc, PANI/NiPPc is depositing only in very thin films. The proton transport was found to be responsible for maintaining the electroneutrality inside the film during cycling.[199] The conductivity for PANI/CoPC composites decreases from that of pure PANI, PANI/PVC, or PANI/PMMA.[200]

Few examples exist for the use of ICP/phthalocyanine composites in chemical sensors. Polyaniline/Cu−phthalocyanine (PANI/CuPc), polypyrrole/Cu−phthalocyanine (PPy/CuPc), and polythiophene/Cu−phthalocyanine (PT/CuPc) have all been examined as gas sensors for vapors such as methanol, ammonia, and nitrogen dioxide. These composites have limited sensitivity to methanol or ammonia gas. However, all polymer composites showed enhanced sensitivity to gas vapors relative to the conductive polymer alone. Increases in analytical sensitivities with respect to nitrogen dioxide gas were on the order of 10^3 depending on the phthalocyanine concentration in the composite. The study neglects discussing or demonstrating the enhanced properties of the composite relative to phthalocyanine films without the polymer.

PANI/phthalocyanines (PANI/MePc, Me = Fe, Ni, or Cu), prepared by a layer-by-layer (LBL) method, have been used to detect dopamine by cyclic voltammetry.[201] Composites produced using PANI/PcFe demonstrated superior sensing properties for dopamine in comparison to polyvinyl chloride/phthalocyanine or PANI/NiPc or PANI/CuPc. The concentration range accessible for PANI/FePc composite was from 0.25 to 8 mM, and the detection limit was 1.0×10^{-4} M. Differences in the voltammetric response were observed as the metal center of the phthalocyanine composites was changed. However, all materials were able to distinguish the dopamine from ascorbic acid based on electrochemical oxidation of the species. The membranes are extremely stable, showing little chemical degradation of the composite after multiple sensing experiments.

The use of metallophthalocyanine as a component of polymeric membrane ion-selective electrodes has the advantages that the active component is not leaching out and does not readily decompose. Modified carbon electrode with hybrid films of poly(*o*-aminophenol) and nickel sulfonated phthalocyanine produced by electrochemical polymerization of *o*-aminophenol in the presence of the metal complex has been used in electrochemical sensors for nitric oxide detection.[202] The oxidation peak current is linear with concentrations up to 200 μM of NO. Overall, phthalocyanines show promise as chemical sensor materials because they are stable with reactive centers that allow the sensing properties to be manipulated, and they can easily be incorporated into ICPs. However, further studies are required to fully adapt these macrocyclic materials to composite materials for chemical sensing.

3.4. Composites with Biological Materials

The emerging trends in biosensors based on ICPs, covering approximately the last 5 years, have been described in the literature.[203] Various methods have been investigated for biosensing applications using ICP and biomaterials composites. In contrast to environmental-based sensing, the materials used to create the composite must be biocompatible to be used in vivo. These materials should be inert and provide high loading of the biologically specific component with minimal leaching. A recent review has been presented regarding the advantage of ICP membrane-based biosensors.[204] Although biosensing continues to expand encompassing enzymatic systems, proteins (amino acids), DNA, antibodies, and antigens, the vast majority of systems incorporate enzymes and the biologically active material. These systems use enzymes that are affixed, immobilized, or encapsulated in a variety of matrix materials.

The primary advantages of ICPs over other possible matrices include the enhanced speed, stability, and sensitivity of enzyme biosensors. Incorporation of single enzymes or groups of enzymes provides the biosensor selectivity to either single or multiple biological components. The ICP acts as the transducer, converting the chemical response into electric current. Synthesis of the material usually involves chemical or electrochemical polymerization in the presence of an enzyme. However, in some cases the polymers functional groups can be used to covalently attach the enzyme to the matrix. Common analytes include species such as glucose, cholesterol, urea, and uric acid due to their biological relevance with respect to the health of an individual. A few examples are provided to demonstrate how conductive polymer/enzyme composites have been utilized for biosensing applications.

Use of ICPs in the design of bioanalytical sensors has primarily focused on polypyrrole (PPy) and polyaniline (PANI) because they are biologically compatible and do not dissolve in water. Immobilization of biologically active molecules within PPy during electrochemical polymerization has been examined.[205] The polymers have also gained recognition in the field of mimicking natural sensing organs by combining electromechanical actuators with the ability to control biological processes in drug delivery systems.[206]

Daily glucose monitoring is an important factor in the management of diabetes. The enzyme, glucose oxidase, has been successfully incorporated into chitosan-PANI membranes.[207] Inclusion of chitosan provides chemical-binding sites to affix the enzyme, increases the stability, and prevents leaching of the enzyme. A near linear increase in the current associated with 5 mM glucose is observed for the layer-by-layer growth of chitosan/polyaniline/glucose oxidase sensor. The current associated with glucose oxidation is not saturated over the first 12 layers. The sensor produced using 12 layers shows linearity in the concentration range from 0.5 to 16 mM. In comparison to the chitosan/glucose oxidase sensors, inclusion of PANI increases the dynamic concentration range and decreases the time required to reach the steady-state response by a factor of 2.

Amperometric biosensors have been prepared using conducive polymers such as PANI and PPy with the enzyme tyrosinase.[208] Tyrosinase is used to monitor the oxidation of phenolic residues that can be found in air, soil, and water. The release of phenol compounds is typically associated with decomposition of plastics and plasticides, pesticides, and paper processing. Phenolic residues are easily absorbed in humans through ingestion, transdermal uptake, and inhalation. The enzymatic response of a PANI/tyrosinase composite membrane is demonstrated for phenol. Although the authors demonstrate that the composite can be used in the oxidative detection of phenolic species, they fail to fully evaluate the figures of merit for the sensor material. Specifically, the authors do not evaluate the dynamic concentration range, limit of detection, and analytical sensitivity. In contrast the PPy/tyrosinase composite was fully characterized with respect to phenol, catechol, and *p*-chlorophenol. The PPy/tyrosinase sensor was sensitive to phenol, catechol, and *p*-chlorophenol over concentration ranges from 9.9 to 84.7, 6.7 to 72.6, and 3.9 to 48.8 mM, respectively. Sensitivities for phenol, catechol, and *p*-chlorophenol of 0.14, 0.21, and 0.36 A M^{-1} cm^{-2} were obtained. Detection limits for the three components were between 1 and 2 mM, much lower than previous examples of tyrosinase sensors in the literature. Finally, the long-term stability of the PPy/tyrosinase was found to be superior to conventional biosensors used for detection of phenolic residues.

The link between high cholesterol and heart disease has provided the impetus required for development of cholesterol biosensors. Composites of conductive polymer with the enzymes cholesterol esterase and cholesterol oxidase have been utilized as biosensors.[209] The studies provide a simple method for producing cholesterol sensors that are thermally and chemically stable with good analytical sensitivity. In both studies the enzyme is covalently linked to prevent enzymatic leaching in solution. In addition, the covalent linkages improve the stability of the sensor over a 5 week period. The optimum pH range for detection of cholesterol oleate was determined to be between 7.0 and 7.5 in these studies. Temperature also influences the sensor response with optimum conditions observed at 45 °C. These studies provided a dynamic concentration range of 1−500 mg/dL, a detection limit of 25 mg/dL, and analytical sensitivity of 0.042 mA $(mg/dL)^{-1}$ for the conductive polymer/enzyme composite sensors.

Incorporation of uricase into conducting polymers for evaluation of uric acid biological samples has been examined. In the first study, polyaniline was synthesized in the ionic liquid 1-ethyl-3-methylimidazolium-ethyl sulfate (EMIES).[210]

The conductive polymer membranes prepared in the ionic solution show high electric conductivity up to pH values of 12. In addition, the polymer has been shown to have high flexibility and good mechanical properties. Acetaminophen, glutathione, L-cysteine, and ascorbic acid were combined with solutions containing uric acid (0.5 mmol dm^{-3}) and compared to the response of uric acid alone. The biosensor composites produced from PANI/uricase prepared in ionic liquid are resistant to interference and impurities in comparison to PANI/uricase prepared in acid solutions. The sensor displays a linear dynamic concentration range of uric acid between 1.0×10^{-3} and 1.0 mmol dm^{-3}. The authors do not provide a measure of the analytical sensitivity of the composite prepared in ionic liquid. However, the response is significantly enhanced relative to uric acid sensing using PANI prepared in acid. Although the authors state that uricase is immobilized in the polymer matrix, the enzyme actually acts as a dopant, with no covalent contact with polymer.

Immobilization of uricase into PANI membranes has also been achieved, and the biosensing of uric acid has been evaluated using the composite.[211] Covalent bonding of uricase is achieved in PANI using glutaraldehyde as a cross-linker. The covalent bond keeps the enzyme immobilized in the polymer matrix and enhances the stability of the sensor membrane, remaining 95% active after 18 weeks. The authors also demonstrate that the composite with immobilized uricase is superior to PANI/uricase composite produced through simple doping of the polymer. The response of the composite to uric acid displays two linear ranges with respect to concentration between 0.01 and 0.05 mM and 0.1 and 0.6 mM. The analytical sensitivity obtained from the calibration is 47.2 mA nM^{-1} at low concentrations and 10.66 mA nM^{-1} at higher concentrations. Optimum results are obtained at temperatures between 30 and 35 °C and pH values of 6.5 with limited activity up to pH 8. The influence of possible interference from other biologically relevant species was also examined using the PANI/uricase composite. The sensor showed little activity with respect to urea, glucose, ascorbic acid, cholesterol, and lactic acid. The authors also examined serum samples using the composite and compared the results to spectroscopic measurement of uric acid. The results are very similar, indicating the composite can measure uric acid in real biological samples.

4. Conclusions and Outlook

This review of the trends in the synthesis and application of ICP composites in chemical sensing demonstrates the versatility of these materials. It highlights the concept that rational design of composites can be utilized to develop novel sensing materials with improved properties such as enhanced resistance to humidity, lower detection limits, increased sensitivity, lower sensing temperatures, and enhanced stability. The simple application of combinatorial chemistry techniques can be used to produce large volumes of sensor material. However, this approach does not represent the rational design of composite sensors. Rational design requires that a more fundamental understanding of the properties of the ICP and secondary component be evaluated independently and as a combined entity. Knowledge of the individual materials and the changes associated with the combined species provides the necessary guidance for enhancing favorable and reducing unfavorable attributes. The design of a sensor can only proceed with a fundamental understanding of the chemical, physical, and mechanical properties of the composite materials. When these parameters are understood they can be utilized to develop sensors with designed reactivity, sensitivity, and selectivity.

It is apparent that not all of the unique, tunable properties that are observed in composite materials have been utilized for chemical sensor applications. However, the enhanced properties of the composites, relative to each of the individual material, have been used extensively in other applications including batteries, fuel cells, and catalyst. In addition, the extensive knowledge of functional components including organized mixed monolayers on gold nanoparticles is just starting to be applied to the design of diverse sensors.

Furthermore, a complete understanding of the properties of the individual components influence the sensing properties of the composite has not been extensively studied. For example, charge propagation in the composite, the limits of charge mobility through the composite, the true effect of water vapor, oxygen, or light on the interaction of analyte with the composite, and how the applied processing method of the composite influences the properties are all factors that must be addressed. The rational development of composite materials that provide enhanced sensing capabilities should use standardized methods for evaluation of ICP and ICP composites, respectively. This approach would allow comparison of sensing results achieved with different layers and also could contribute to the rapid progression of the design and implementation of novel materials in sensing applications.

Further developments in metal nanomaterials and their electronic properties, chemical functionalization, and catalytic properties will continue to impact the sensor field. Development of methodologies to control the shape, size, and range of distribution of CNTs and metal clusters within ICP matrices is required. In addition, characterization of the chemical and physical properties of ICP composite is required to fully understand the influence of secondary components on the sensing properties. It is impossible to control the properties of the secondary component if the properties of the ICP matrix are not fully understood. Identification of new properties of nanomaterials requires new methods for the preparation or assembly of usable composite structures. The work of Penner and co-workers is an example that demonstrates how new methods can be utilized in the preparation of naked (palladium) and bimetallic beaded nanowires ranging in diameter from tens of nanometers to 1 μm. These materials are used in the detection of hydrogen gas.[212] Further work is required to develop applications for structured nanowire materials. In contrast to CNTs and in spite of the enormous progress in synthesizing and structural characterization of metal oxide nanowires such as SnO_2, ZnO, and TiO_2, few of these structured materials have been utilized in gas sensors for detection of common gases such as CO,[213] O_2,[214] or water vapor.[215] The advantages of metal oxides have been shown with respect to lowering the required operation temperature of the analytical sensor.

Implementation of new building blocks that can be used to assemble 1-D nanowires[216] or nanoparticles to produce 2-D nanofilms[217] have been reviewed but not yet implemented in the design of novel ICP composites. There has been progress in making supercrystals that are produced from rare-earth oxides M_2O_3 (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy) that are uniformly and spontaneously assembled to form nanorods, nanowires, and nanoplates.[218] Ultranarrow semiconductors (ZnS, ZnSe, CdS, CdSe) with tunable subnanometer increments have been produced using microwave irradiation.[219] Nanorods with a controllable interparticle spacing have been achieved using capping agents of varying alkyl chain lengths.[220] In addition, the recently developed theoretical description of the evolution of an ensemble of nanoparticles in colloidal solution used to control the nanocrystal monodispersity of semiconductors and magnetic alloy nanocrystals as building blocks of 2-D and 3-D arrays and colloidal supercrystals should find application in developing advanced sensing layers.[221] These studies highlight the advancement of synthetic methods to produce new, unique materials that can be utilized to produce new composite materials.

New electronic, optical, and mechanical properties that are interesting to solid-state electrochemical and optical sensors may be obtained from inorganic fullerene-like WS_2 and MoS_2 polyhedra and nanotubes which are capable of modulating the energy gap with shrinking diameter. In this respect they are prevalent as compared to many of the bulk 2D materials because they exhibit a direct gap rather than an indirect gap transition.[222] Their thermodynamic stability and the ability to fine tune the Fermi level by doping and intercalation of metal atoms makes them novel materials for sensor applications because their catalytic properties can be controlled.[223]

In summary, the next generation of ICP materials for chemical sensors should be able to balance their processability with their sensing performance with regard to faster response times, sensitivity, selectivity, lower detection limits, and larger dynamic concentration ranges. It should be feasible to control the molecular structure and morphology when the material is processed in order to address the issue of analyte sorption and diffusion. Additionally, controlling or tailoring the properties of the interface can be used to minimize charge trapping and contact resistance within the sensor device structure. Any sensor should incorporate an understanding of the properties of each component independently while evaluating the new properties of the composite. Rational sensor design that utilizes the combined chemical, physical, and mechanical properties of the composite materials is crucial in the development of selective, sensitive sensing mechanisms.

5. Acknowledgments

This work was supported by the NSF Grant CHE 0452045 (M.J.) and DOE Grant DE-FG36-05GO85028 (D.W.H.).

6. References

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CR068112H