

Application and Basic Concept of Conducting Polymers for Environmental Protection

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Abstract

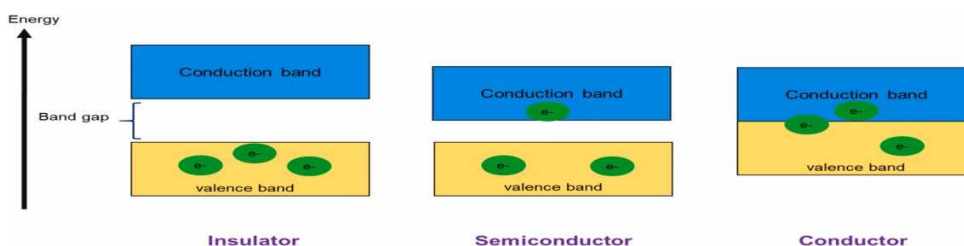
Recently, the importance of sustainable environment has been engaged in many science practices and learning. This article intends to provide teachers in secondary school and research beginners with knowledge background on conducting polymers (CPs) for its application in environmental protection studies. A concise and straightforward discussion on the basic concept of CPs and its role as i) sensors for gas pollutants ii) photo catalyst are explained. A general workflow to guide readers in identifying and validating suitable sensors is included. In addition, the article provides a step-by-step guideline to assist readers in performing photo catalytic degradation experiments associated with CPs.

Keywords: Conducting polymer, electron, environment, photocatalyst, and sensor.

Introduction:

Does polymer conduct electricity

To answer this question, first the reader should have some basic understanding on the concept of electronic conductance. In general, the electronic conduction is described as the movement of Free State electron(s) or charges under potential gradient producing current. The electronic conductivity of a material is reliant on the opportunity for electron(s) excitement from the valence band towards the conductance band (Figure 1).



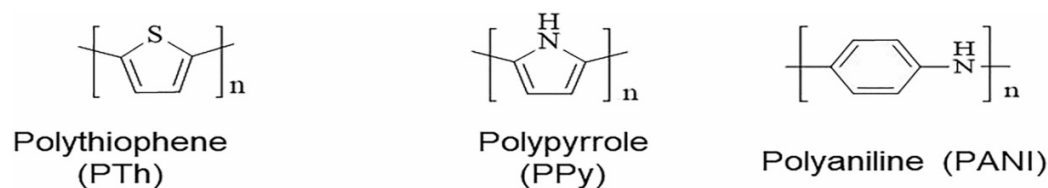
Insulator, semiconductor and conductor.

Most metals have no or lack of barrier (often termed as band gap) between the valence and conduction band hence creating a highly conductive condition. Moreover, orbital overlapping in metals also promotes movement of electron(s) towards the conductance band. Meanwhile, for those substances with appreciative band gap size, this electron flux is restricted or non-achievable, therefore the materials are considered either as semiconductors (depending on the bandwidth size) or insulator (Shahabuddin et al., 2018)

Polymer, in general, is a long-chain organic macromolecule made up of linking monomers that are associated with carbon chain molecules. The aliphatic carbon chain that constitutes most parts of polymers has complete filled electron(s) in their octet configuration of the covalent bonding. Thus, most polymers beforehand are considered as insulator (non-conductor) due to the non-availability of free electron(s), which is prudent to create the electronic conductivity as described earlier. However, in the seventies, a new class of polymer that conducts electricity was discovered by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa (Shirakawa, Louis, & Macdiarmid, 1977) leading to the Year 2000 Nobel Prize Award in Chemistry. The discoveries of this “synthetic metal” led to the “dawn of the new plastic age” phenomena and the interest in conducting polymers (CPs) has loomed large since. A detailed explanation on the concept of electronic conduction in polymer has been well discussed in a recently published work by Luscombe, Maitra, Walter, and Wiedmer (2021) Herein, this article will systematically describe some guidelines to use conducting polymer in environmental studies with special focus on its application as sensors and photocatalysis.

What are the examples of conducting polymers (CPs)?

The most common CPs in the literature are polythiophene (PTh), polypyrrole (PPy) and polyaniline (PANI) (Figure 2).



Structure of PTH, PPy and PANI.

Meanwhile, Figure 3 shows the conductivity range of these CPs in comparison to other materials, which falls in the middle range between the semiconductors and metals (conductor)

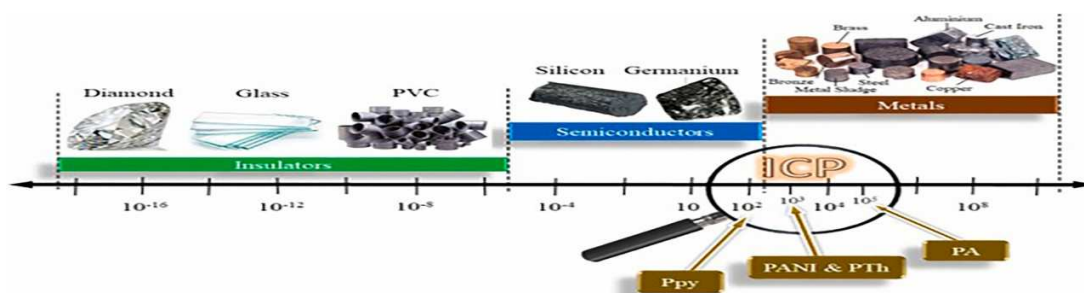
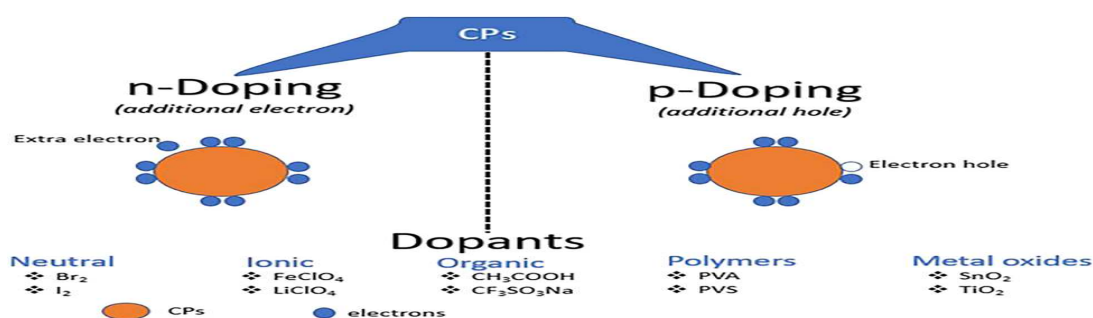


Figure 3:

The comparison of conductivity between CP and other material (Shahabuddin, Mazlan, Baharin, & Sambasevam, 2021).

PANI, PPy and PTh are conjugated polymers with cyclic (aromatic) structure (Figure 2) This cyclic feature is advantageous than those aliphatic structures due to the delocalization of electrons in the π -bonded network within the conjugated bonds that allows for doping process (Engel & Reid, 2010). Doping is an electron reduction (known as p-doping) or electron addition (known as n-doping) process. Figure 4 exhibits the two typical protocols of the n-doping and p-doping process. The choice of dopants ranged from neutral molecules, ionic, organic, or even polymers themselves. The p-doped CPs create electron holes, allowing electron jumps on the π -bond and across the polymeric chain. The n-type doped CPs are very scarce in literature due to their instability of organic anions during the doping process, especially of carbanions. Such species are easy to oxidize upon contact with air or water; thus making the synthesis conditions more challenging.



Types of dopants used in n-doping and p-doping of CP materials (Shahabuddin et al., 2021).

The global need for environmental protection

Environmental conservation and water security are among the two pillars that support the mission of the United Nations 2030 Agenda for Sustainable Development. The world population is expected to grow up to 6.47 billion people from the 3.9 billion as forecasted from 2014 (Jensen & Wu, 2018). Without proper monitoring and regulation adherence towards environment conservation, population and industrial growth are the sources of environmental impacts such as water pollution (Peña-Guzmán et al., 2019), climate change, soil erosion and other ecosystem issues. Anthropogenic factors, like domestic activities and improper discharge of effluent from industries, can generate a wide range of pollutants like toxic heavy metals, synthetic dyes, oil and grease, and toxic gaseous into the atmosphere, soil, and water resources (Rashid, Mazlan, Sapari, Raov Ramachandran, & Pandian Sambasevam, 2018; Shahabuddin et al., 2015). Besides that, ubiquitous pollutants especially from the pharmaceuticals and manufacturing industries like Bisphenol A (BPA), phthalates, and resistance antibiotics are categorized as emerging pollutants. Environmental remediation often involves high capital and operating cost. Hence, reliable and efficient environmental clean-up technologies with economic merit are of great concern.

What is/are the environmental application(s) of conducting polymers?

CPs are used in many environmental applications such as electronics and energy storage devices, corrosion inhibitors, pollutant degradation, electromagnetic interference shielding materials, and sensors (Azim & Venkatachari, 2007; Kalidasan et al., 2021; Koh, Sambasevam, Yahya, & Phang, 2013; Mohd Norsham et al., 2020; Shah et al., 2021). This material has good mechanical strength and exhibits high magnetic properties, unique optical features as well as good electrochemical characteristics (Syed, 2016). Excellent light absorption is also an advantage property of CPs, in which it can act as a transporting material in visible-light excitation state thus improving the photovoltaic efficiency. In this article, we will discuss two most important environmental applications of CPs; which are a) gas sensor, and b) photocatalyst.

Conducting polymer as a sensor for detection of gaseous pollutant

Gaseous hydronitrogen compounds like ammonia (NH_3) and hydrazine (N_2H_4) could be released to the environment through agricultural activities, manufacturing industries and military activities. Excessive ammonia emission could cause adverse biodiversity impacts through soil acidification and damage the human respiratory systems. In addition, atmospheric ammonia could interact with other compounds in air contributing to the formation of harmful fine particulate matter (PM_{2.5}). Hydrazine meanwhile is a highly reactive, toxic and flammable odorless gas; hence is difficult to trace. To detect and monitor the concentration level of these gaseous pollutants, sensor technology is one of the mitigation strategies for air pollution control .

In general, sensor is a device that converts the input (i.e., physical changes) into an electrical signal that could be read at an output instrument.. Such physical changes include the alteration of pH sensitivity, affinity towards inorganic ions, organic molecules, and selected gas species .Gas species interact with the conducting polymer sensors via two major mechanisms: chemical interaction or physical adsorption. Chemical interaction involves the alteration of the doping level via the oxidation process. Gas species with higher electron affinity than CPs (e.g., NO_2 , I_2 , O_3 , and O_2) are capable of oxidizing the CPs and later increase their doping level. This alteration will change the physical properties of the CPs (like its resistance or optical absorption) that will be converted to the response to electronic signal and reading measurement in the sensor. On the other hand, CPs synthesized with metal composites tend to form the n-p heterojunction with a depletion region that allows the uptake of the gaseous molecules. Some gas species exhibit weak physical interactions of non-reactive volatile organic compounds such as chloroform, acetone, and benzene. Thus, the physical adsorption of these gas species would modulate the overall conductivity of the CPs.

Modification of pristine CPs is very much anticipated to boost their performance, retain their stability, reduce the cost, and offer more versatile features. If the reader would like to design or modify CPs as a gas sensor for their own research or project assignment, we recommend the reader to choose a CPs sensor which works based on resistivity

changes. This type of sensor is most used for pollutant detection that works on sensitivity factor as the principal monitoring tool.

Herein we suggest the readers (teacher or research beginners) to adopt the suggested framework (Figure 5) for the selection of suitable CPs as gas sensors. The sensor response will be denoted as %Sensitivity (%S) where it will be normalized against initial resistance or conductivity collected by the sensor. Typically, evaluation of %S for any CP consists of three components: i) sensor measurement, ii) method validation and iii) sensor performance (Figure 5). Amongst these, sensor measurement is the primary factor to screen and deduce the reliability of modified CP against its pristine material. Next, method validation provides an insight on the true performance of a sensor where it should exhibit linearity with a correlation coefficient (R^2) more than 0.99 or close to unity.

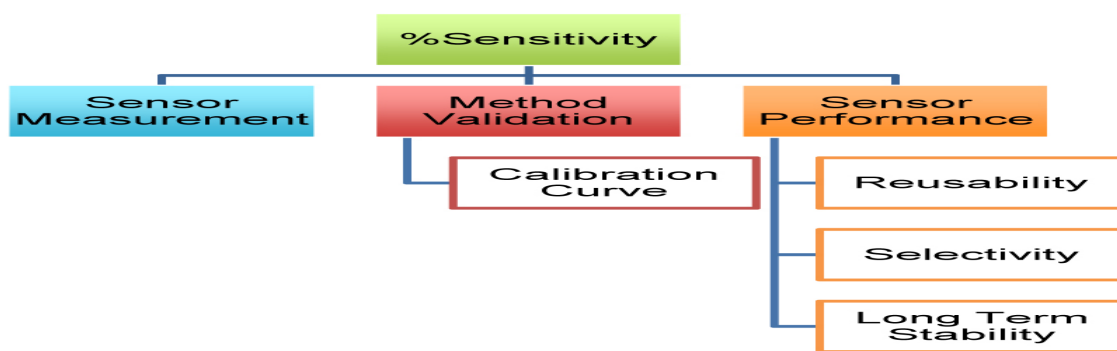
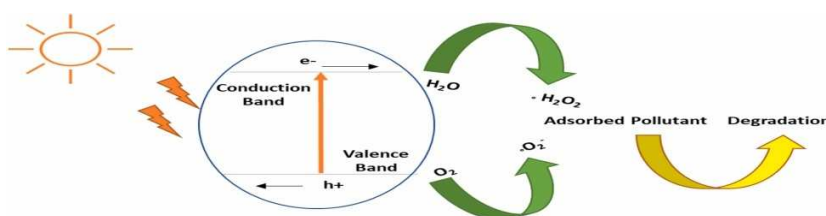


Figure 5:
Flowchart on simple methodology for CPs sensor evaluation for pollutants.

Finally, it is of paramount interest for every sensor to validate its performance in terms of reusability, selectivity, or sometimes denoted as interference study and long-term stability. Generally, the cut off %S values for any sensor performance studies shall not be less than 90%. Reusability signifies how many times a CPs' sensor could be reused in a single day. High reusability could reduce the cost incurred for sensor manufacturing and waste build-up. The selectivity study describes the favorability towards each pollutant; often measured by the ratio of the response of the sensors to each of the targeted pollutants. The sensitivity response could be visualized in a plotted bar chart by showing a comparison between the target pollutant and other common interfering species from the tested conditions.



Basic principle of photocatalysis.

A metal-oxide semiconductor is the most suitable photocatalyst for the degradation of pollutants ascribed to its suitable band gap position, non-toxicity, low cost, chemical and photonic stability, and biocompatibility. However, despite its excellent physicochemical properties, bare metal oxide has limited photocatalytic efficiency, due to the rapid recombination rate of photogenerated electron-hole pairs within the metal oxide particles. Therefore, conducting polymer is combined with a semiconductor material to act as an important inhibitor of electron-hole pair recombination. CPs that are mostly studied by researchers for photocatalytic activity are polyacetylene (PA), polyaniline (PANI), polythiophene (PTh) and polypyrrole (PPy). As explained earlier, CPs (with conjugated structure) are rich in delocalized and mobile π electrons throughout their polymeric chain. Conjugated polymers, therefore, are a good light harvester and promote carrier separation in photocatalytic composites that eventually increase the degradation efficiency. Moreover, CPs are easy to synthesize and stable in the environment.

Quick guideline for performing photocatalytic experiment using conducting polymer-based material

Herein we include a basic step-by-step approach to design procedure for the photocatalyst experiment. Certainly, research methodology elements such as the identification of research problems, construction of hypothesis and research objectives, review of literature, and conceptualization of research design shall be first carried out for scientific works ; in which are not the focus of this paper. Our aim here is to provide an overview of experimental set-up to assist readers planning to perform a photocatalytic experiment, particularly for the degradation of organic water pollutants. The process involves the following steps:

1. *Identifying the pollutant of interest and type of photocatalyst to be used*

To choose the pollutant, one should take note of factors like the pollutant's solubility (hydrophilic/hydrophobic), chemical speciation, handling issues, and level of toxicity, environmental impact and any emerging issues of the pollutant. Meanwhile, to further understand the physico-chemical characteristics of the photocatalyst (e.g., surface area, thermal behavior, crystallinity) sufficient characterization via spectroscopic, macroscopic, and semi-analytical techniques shall be arranged in the dedicated instrumentation laboratories. The Fourier Transform Infrared, X-ray Diffraction, Scanning Electron Microscopy, and Thermo gravimetric Analysis are some examples of characterization method that usually being used for this purpose.

1. *Determining the experimental conditions or variables that may affect the efficiency of the photocatalytic reaction*

In general, variables like amount of material per volume (loading), pH, type of light source (UV or visible), contact time, and initial pollutant concentration need to be identified. The influence of these variables on photocatalytic reaction has been well described in many previous research articles .Optimization of the experimental variables for a maximum photocatalyst performance could later be performed with the help of

statistical and modeling approaches like the Response Surface Methodology, Taguchi method, Box-Behnken design, etc.

1. ***Selecting appropriate method for data collection (i.e., to measure the concentration of pollutant)***

One should consider the suitable instrument or technique for the data collection (either as qualitative and/or quantitative) of the pollutant of interest. Accuracy, sensitivity, selectivity, availability, handling procedure, and operation cost need to be considered before the experiment execution. UV-Visible spectrophotometer, for example, is a cheap, simple and reliable instrument for measuring highly conjugated organic compounds or chromophores; however, it has drawbacks like low selectivity. On the other hand, Gas Chromatography-Mass Spectrometry (GC-MS) technique has a high selectivity, good sensitivity but is more expensive.

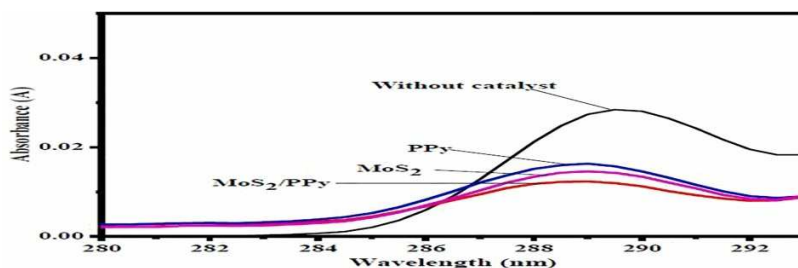
Performing the experiment

To correctly measure the photocatalyst efficiency, experiments will need to be performed in dark condition and then are compared with the presence of light source (e.g., UV light, sunlight). The dark condition is important because some pollutants may self-degrade under exposure to light irradiation. An industrial-designed photocatalytic reactor may work best for ensuring this dark condition. However, if resources are limited, researchers could consider any low-cost approach to prevent exposure to visible light; for example using a self-made dark box or wrapping the reaction container with aluminum foil.

If the photocatalyst is a composite, or in a modified form, it is best to include the pristine (or unmodified material) to be assessed together in the photodegradation experiment. This is to ensure a more significant and valid interpretation of the performance results of the modified material. Most composites may have different or more complex characteristics (e.g., surface area, reactive sites, and morphologies) from their original counterpart.

Analysis and data interpretation

To elucidate the process, we use results from a photocatalytic experiment involving a conducting polymer-metal oxide composite made of polypyrrole (PPy) and molybdenum disulfide (MoS_2) as an example. The composite (PPy/ MoS_2) was used for the degradation of an organic pollutant 2-chlorophenol and was compared with its pristine materials (PPy and MoS_2 , respectively). Using a UV-Visible spectrophotometer, the concentration of 2-chlorophenol remaining after the photodegradation experiment was measured and reported as Absorbance, A, as illustrated in Figure 8.



Different absorbance value (A) for different catalysts (experimental condition: loading = 0.01 g nanocomposite in 5 mL of 50 mg/L 2-chlorophenol, pH = 5, exposure time to sunlight = 3 h).

Source (Kasim, Baharin, Yunus, Shahabuddin, & Noor, 2020).

In spectroscopic quantitative analysis, the fundamental relationship between the absorbance (A) and concentration (c) of an adsorbing medium in a specific optical path length of radiation (cell thickness) is described by the Beer–Lambert Law (Engel and Reid, 2010, Housecroft and Constable, 2010). According to this law, the value of absorbance has a linear relationship with the concentration provided that the cell thickness and radiation wavelength remains constant. Thus, the solution's concentration could be calculated once the absorbance value is measured. The interpretation of the result obtained in Figure 8 is as follows:

1. The control experiment serves as the standard that minimizes the effect of other experimental variables other than the factor of interest (in this case the choice of photocatalyst either Ppy, MoS₂ or PPy/MoS₂). The control experiment (no photocatalyst added) showed the highest absorbance value that represents the original concentration of 2-chlorophenol (before degradation).
2. For each PPy, MoS₂ and PPy/MoS₂, the height of absorbance peak was greatly declined (almost 50% height reduction). The decrease in the absorbance peak indicates a lower concentration of 2-chlorophenol remains in the measuring system. Thus, both conducting polymer (PPy), metal oxide (MoS₂) and composite (PPy/MoS₂) were considered successful in degrading the 2-chlorophenol.
3. In accordance with the height of absorbance peak of the 2-chlorophenol, the degradation efficiency is in the order of PPy/MoS₂ > MoS₂ > PPy. The composite is a better photocatalyst as compared to the pristine material. The synergetic effect between PPy (conjugated bond) and MoS₂ (low bandgap) combined in the composite has created more reactive species in an aqueous solution that stimulates more photodegradation of 2-chlorophenol.

In more advanced studies, experimental variables (e.g., the light intensity and initial pollutant concentration) and the properties of the conducting polymer (e.g., surface area, bulk density, conductance) are further analyzed to establish the kinetics profile, mechanism, and scale-up studies. More sophisticated surface and atomic level characterization techniques, modeling or experimental design approach are hence necessary.

Conclusions

In this paper, we have included a brief concept of conducting polymer and its application in environmental remediation with special highlights on gaseous sensors and photocatalytic material for the degradation of water pollutants. The topic is described in a concise and straightforward approach aiming to assist teachers in search of relevant teaching reference pertaining to the conducting polymer field. This article is also equipped with a proposed guideline for selecting suitable gas sensors and procedure for photocatalytic experiment to be practiced by research beginners. It is a great hope that this work could stimulate more learning and research interest in the field of polymer as a roadmap for the achievement of the United Nations Sustainable Development Goals agenda.

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