A PHOTOCURABLE METHOD FOR COPPER(II) OXIDE-DOPED POLYANILINE CONDUCTING POLYMER MEMBRANE SYNTHESIS

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ABSTRACT

The development of conductive polyaniline (PANI) membrane doped with copper(II) oxide (CuO) by means of the photocopolymerization method has been successfully carried out. The photocurable PANI polymeric material was synthesized by mixing 0.011 g of aniline monomer with 0.016 g of ethylene glycol dimethacrylate (EGDMA) crosslinker, 0.021 g of dimethoxy phenylacetophenone (DMPP) photoinitiator and 0.026 g of CuO dopant. The electrical conductivity analysis showed that the as-synthesized CuO-doped PANI (PANI/CuO) film possessed an optimum electrical conductivity value of 39.81×10^{-3} S cm^{-1} at the dopant loading of 0.011 g CuO. Chemical elucidation by using Fourier-transform infrared spectroscopy (FTIR) revealed that the PANI/CuO conducting material with several main functional groups e.g., N-H, C-H, C-N, C=C, C=N, C-O and C=O chemical bonds were identified. Meanwhile, optical characterization of the resulting PANI/CuO membrane by using UV–vis diffuse reflectance spectrophotometer (DR/UV-vis) showed that PANI underwent electron transition π-π* (C=C) at a wavelength of 324 nm, and band gap values of 2.35 eV, 1.33 eV, 1.39 eV, 1.42 eV, 1.42 eV, and 1.50 eV for PANI, PANI/CuO 0.011 g, PANI/CuO 0.016 g, PANI/CuO 0.021 g, PANI/CuO 0.026 g, and CuO, respectively.

Keywords: doped polyaniline, conducting polymer, photopolymerization, conductivity, band gap.

INTRODUCTION

The development and characterization of conductive polymers have become one of the most sought-after studies because it is widely applied and application, especially as biosensors or chemical sensors material support. Conducting polymers are different from non-conducting polymers in general which are insulators. Intrinsically conductive polymers (ICPs) are organic polymers that are able to conduct electric currents comparable to conventional metals and semiconductor materials1. Several conductive polymers that are often used for sensors include polypyrrole, polyiophene, polycetylene, and polyaniline (PANI)2. Of various examples of conductive polymers, PANI is known as one of the interesting materials to study because of its easy synthesis process, good environmental stability, and high electrical conductivity3. Furthermore, PANI can be applied to chemical and biological sensor devices, light-emitting devices, electrodes, battery manufacture, corrosion protection, and solar cells4. PANI can be produced from the polymerization of aniline monomers with a regular polymer structure by chemical and electrochemical routes with alternating phenyl rings and containing nitrogen groups4. In addition, many studies on the
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synthesis of polyaniline incorporated dopant materials to improve the electrical conductivity of PANI. The concentration and types of dopant used have been observed to affect the charge carriers and electrical conductivity of the resulting polymers. Several types of metal oxides can be used as dopants, such as ZnO, TiO₂, SnO₂, Fe₂O₃, and CuO. Research conducted by Huang synthesized PANI doped with Zn²⁺ and Cu²⁺ ions by chemical polymerization using H₂O₂ as an oxidant. The polymerization reaction was initiated by slowly heating the mixture to 50 °C for 3 h, which is stirred continuously. The mixture was then cooled at room temperature until a precipitate formed. The transition metal was incorporated into the polymer via coordinate covalent bonds between the transition metal ion and the PANI polymeric chain with the electrical conductivity of the metal ion coordinated PANI appreciably increased compared to non-doped PANI. In a separate study carried out by Bai who synthesized PANI doped with metal oxide of Ni₂O₃ and ammonium persulfate as oxidant. An increase in the electrical conductivity was discerned along with the increase in the amount of Ni₂O₃ used. However, the PANI synthesis process recommended by both Huang and Bai is taking a long time to produce PANI in the form of powder. In this research, PANI (PANI/CuO) doped with CuO has been developed through a photopolymerization reaction under exposure to UV radiation to produce ICP thin films. The precursor comprised aniline, ethylene glycol dimethacrylate (EGDMA), CuO dopant, and 2,2 dimethoxy-2-phenylacetophenone (DMPP) as photoinitiator. The proposed photopolymerization method is safe and environmentally friendly with low energy consumption, solvent-free procedure, required ambient synthesis conditions, and relatively low cost.

EXPERIMENTAL

Instruments and Chemicals
The instruments used in this research include a UV light transmitter unit (RS Ltd.), a four-point probe (FPP), Fourier-transform infrared spectroscopy/FTIR (GX infra-red spectrophotometer, Perkin Elmer), and UV–vis diffuse reflectance (DR/UV-vis) spectrophotometer (SPECORD 210 PLUS). While the chemicals used for the synthesis of polyaniline (PANI) are 2,2 dimethoxy-2-phenylacetophenone (DMPP), aniline, ethylene glycol dimethacrylate (EGDMA), and copper(II) oxide (CuO). These chemicals were purchased from Sigma-Aldrich.

CuO-doped Polyaniline Synthesis
The CuO-doped polyaniline (PANI/CuO) was synthesized via the photopolymerization method based on previously reported procedures with some modifications. The precursor polymers at different dopant loadings were made from the reaction of 0.03 g DMPP with 300 μL EGDMA, 300 μL aniline, and CuO at 0.011 g, 0.016 g, 0.021 g, or 0.026 g. These mixtures were sonicated until homogeneous and photopolymerized using UV-light for 10 min. This mixture was prepared under nitrogen gas flow. A control PANI i.e., undoped PANI was also prepared without adding CuO. Analysis of molecular functional groups of doped and undoped forms of PANI was performed with FTIR. The interaction of infrared radiation with matter causes a specific atomic vibration in the sample, this vibration will result in the absorption and transmission of certain energy according to the functional groups present in the molecule. The PANI bandgap energies doped and not doped with CuO were identified using a UV-vis (DR/UV-vis) diffuse reflectance spectrophotometer. Diffuse reflectance is radiation that can penetrate into a solid sample and experience scattering (i.e., reflection, refraction, and diffraction in all directions), and the absorption of this radiation depends on the given wavelength. There is a relationship between the band gap and the conduction properties of the material. This band gap can be determined through diffuse reflectance with DR/UV-vis as well as being used as a method for determining the optical properties of samples of powdered nanomaterials, as well as for determining the semiconductor properties of materials. The band gap energy value is determined using the method of Tauc Plot, where the energy absorption coefficient (α) is determined through the equation below:

\[(\alpha.hv)^{1/\gamma} = B(hv - E_g)\]  \(\text{(1)}\)

Where, \(h\), \(v\), \(E_g\), and \(B\) are Planck’s constant, photon frequency, band gap energy, and constant, respectively, and electron transition (1/2 or 2 for direct and indirect band gap). The band gap is determined from the value of the reflectance (%R), which is converted into the Kubelka-Munk factor (F(R) and expressed in the equation below:
\[ F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \]  

(2)

Where, \( K \), \( S \), and \( R \) are absorbance coefficients, scattering coefficients, and reflectance, respectively. The calculated \( F(R) \) value is then substituted into equation 1, resulting in equation 3 as follows:

\[ (F(R)hv)^{1/\gamma} = B(hv - E_g) \]  

(3)

Electrical Conductivity Analysis

The conductivity of PANI/CuO material was analyzed with the FPP method, which measures the resistivity (resistance) value of thin layer material. This method uses four probes, where two probes function to conduct electric current and two other probes to measure the electric voltage with the four probes touching the surface of the material (sample) as shown in Figure-1. The change in voltage is measured from the variation of the given current\(^\text{17}\). The resistance and electrical conductivity of the PANI/CuO are calculated using the following equations:\(^\text{18}\)

\[ \rho = 2 \pi s \frac{V}{I} \]  

(4)

Where \( \rho \) is the resistivity (\( \Omega \)cm), \( \pi \) is the value of the radius (3.14), \( s \) is the distance between the probes (cm), \( v \) is the electric potential difference (volts) and \( I \) is the current strength (A). While the conductivity value is inversely proportional to the resistivity as shown in equation 5.

\[ \sigma = \frac{1}{\rho} \]  

(5)

Where, \( \sigma \) is the conductivity (S/cm) and \( \rho \) is the resistivity (\( \Omega \)cm).

**RESULTS AND DISCUSSION**

FTIR Characterization of PANI and PANI/CuO

Figure-2 show some of the main absorption peaks that appeared in the FTIR spectra of PANI, PANI/CuO 0.011 g, PANI/CuO 0.016 g, PANI/CuO 0.021 g, PANI/CuO 0.026 g and CuO. The wave number of 3373 cm\(^{-1}\) from the PANI and PANI/CuO spectra shows the vibration of the N-H compound. The absorption peak at 2958 cm\(^{-1}\) indicates the vibration energy of the –CH bond. The C=O stretching band at the wavenumber around 1700 cm\(^{-1}\) overlaps with both the ester and ketone functional groups of 1718 cm\(^{-1}\) and 1740 cm\(^{-1}\), respectively. The overlapping absorption peaks are also found at a wavenumber of around 1600 cm\(^{-1}\) i.e., the absorption bands for both C=C and C=N at the 1622 cm\(^{-1}\) and 1685 cm\(^{-1}\) wavenumber, respectively. The absorption peaks at 1255 cm\(^{-1}\) and 1143 cm\(^{-1}\) are attributed to the respective C-N and C-O functional groups. The absorption peak at the wavenumber of 547 cm\(^{-1}\) is due to the CuO bond vibration. There are similarities in the absorption peaks between PANI and PANI/CuO absorption spectra, which were due to the same functional groups that make up both PANI and PANI/CuO. The difference between the PANI and PANI/CuO FTIR spectra appears in the shift of some absorption bands to a larger wavenumber. The absorption peaks of PANI at the wavenumbers of 3373, 2958, 1622, and 1143 cm\(^{-1}\) shifted to 3378, 2962, 1626, and 1147 cm\(^{-1}\) after doping with CuO\(^\text{19}\). The difference in the absorption peaks between PANI and PANI/CuO spectra is ascribed to the different amounts of CuO dopants added. Conjugation of CuO dopant to the PANI also rendered a decrement in the absorption peak intensity, especially in the C=C vibration. This was due to the increase in steric resistance as the CuO mass increases. This barrier can impede the mobility of the charge carriers and cause the conjugate chain to shorten\(^\text{20}\)
### Band Gap Analysis

Figure-3 demonstrates the UV–visible diffuse reflectance spectra of CuO, PANI and PANI/CuO at different CuO loadings from 0.011 g–0.026 g. The DR/UV-vis spectra of all samples are in the UV region (200-400 nm). The CuO spectrum has an absorption peak at the wavelength of 328 nm, which is associated with the π-π* transition (Cu=O), whilst PANI has an absorption peak at 324 nm that indicates the π-π* transition of the benzenoid group (C=C aromatic). The effect of doping on polyaniline properties has also been previously reported by Zhihua. The addition of CuO dopant to PANI resulted in a shift in the DR/UV-vis peak to a shorter wavelength as can be seen in the PANI/CuO 0.011 spectrum. As the CuO loading increased between 0.016 g and 0.026 g, there was a shift in the absorption peak to a longer wavelength within the UV region, which can be correlated to the band gap value.

Figure-4 demonstrates the Tauc plots of various material samples and the band gap values of PANI, PANI/CuO 0.011 g, PANI/CuO 0.016 g, PANI/CuO 0.021 g, PANI/CuO 0.026 g, and CuO acquired at 2.35 eV, 1.33 eV, 1.39 eV, 1.42 eV, 1.42 eV and 1.50 eV, respectively. The PANI's band gap value decreased from 2.35 eV to 1.33 eV after doped with 0.011 g of CuO. The decrement in the band gap value is influenced by the addition of CuO, which has a smaller band gap value than PANI at 1.50 eV. The decrease in the value of band gap of PANI associated with the presence of CuO was ascribed to the formation of intermediate levels between the band gaps, which can lead to an increase in the PANI/CuO electrical conductivity, whereby the electrons excitation from the valence band level to the conduction band.
level through the intermediate level, and resulting in an increase in electrical conductivity and a decrease in the band gap value. However, further increased the CuO loading to the PANI from 0.0016 g to 0.026 g, it heightened the band gap value from 139 eV to 1.42 eV, but it is smaller than the PANI band gap value.

Fig.-4: Tauc plots of various material samples modeled via K-M Model; (a) PANI, (b) PANI/CuO 0.001 g, (c) PANI/CuO 0.0016 g, (d) PANI/CuO 0.021 g, (e) PANI/CuO 0.026 g, (f) CuO

**Electrical Conductivity Analysis**

The conductivity value of PANI/CuO was analyzed with a FPP, which was used to measure the resistivity (resistance) of a thin layer material. FPP analysis was conducted with the four probes placed at the same spacing in a row touching the sample surface. The current was flowed through probe 1 to probe 4 such that the current was distributed laminarily through the sample from one probe to the other. The voltage was measured between the second and the third probe with a voltmeter. The resistivity value of the sample material can be calculated by using equation 4 and equation 5. The conductivity values of PANI and PANI/CuO versus the added mass variation of CuO can be seen in Figure-5a. Compared with PANI, the electrical conductivity of PANI doped with 0.011 g CuO increased from $3.61 \times 10^{-3} S \text{ cm}^{-1}$ to $39.81 \times 10^{-3} S \text{ cm}^{-1}$. The increase in the conductivity value was due to the use of dopants, which affect the density of the charge carriers, whereby the CuO dopants increased the mobility of the charge carriers in PANI. This indicates that there is a strong interaction between CuO and PANI, this interaction causes PANI/CuO to behave like a metal. In addition, the involvement of Cu and O orbitals can increase the density of states in PANI/CuO and increase their conductivity. However, as more and more CuO masses were added, these resulted in a decrease in the conductivity of PANI/CuO from $39.81 \times 10^{-3} S \text{ cm}^{-1}$ to $7.96 \times 10^{-3} S \text{ cm}^{-1}$ as the addition of excess CuO dopants affecting the PANI/CuO density, and inhibiting charge carrier transport in the conduction pathway of the PANI chain. Moreover, the interaction of PANI and excess CuO caused a decrease in the conjugated chain length in PANI. Figure-5b demonstrates that the conductivity of PANI/CuO obtained is influenced by the value of the bandgap of the tested sample, where PANI/CuO with the highest conductivity has the lowest band gap value and vice versa. The conductivity of PANI/CuO is generated by the transfer of electrons from the valence band to the conduction band. This electron transfer is strongly influenced by the bandgap value. The smaller the bandgap value, the easier it is for electrons to be excited from the valence band to the conduction band so as to increase the conductivity value. This study demonstrates, the highest electrical conductivity value was attained by the PANI/CuO doped with 0.011 g CuO with a conductivity of $39.81 \times 10^{-3} S \text{ cm}^{-1}$ and a band gap value of 1.33 eV. Similar electrical conductivity trending related to the band gap is reported by Karaoglan who synthesized PANI by using different types of dopant, e.g. the electrical conductivity results obtained for PANI, PANI/BSA, PANI/HCl,
and PANI/HCl/BSA were 0.00029 S cm\(^{-1}\), 1.39 S cm\(^{-1}\), 0.54 S cm\(^{-1}\), and 0.77 S cm\(^{-1}\); and the band gap values obtained for each sample were 3.06 eV, 2.35 eV, 2.40 eV, and 2.38 eV, respectively\(^{22}\).

**CONCLUSION**

The physicochemical properties of the as-obtained PANI and PANI doped with CuO based on FTIR analysis showed the presence of N-H, C-H, C=O, C=C, C-N, C-O, and Cu=O chemical functional groups. The results of optical DR/UV-vis analysis showed that the band gap value of PANI and PANI/CuO can be influenced by the loading of CuO dopant, which is associated with the electrical conductivity of the resulting intrinsically conductive polymers. The smaller the band gap, the higher the conductivity of the conducting polymer. The smallest band gap with the highest conductivity (39.81×10\(^{-3}\) S cm\(^{-1}\)) was produced by the PANI/CuO doped with 0.011 g CuO in this study. The conjugation between PANI and CuO dopants has caused the band gap value to drop, which in turn increased the conductivity and the number of charge carriers of the resulting PANI/CuO. Therefore, the presence of dopants has significantly improved conductivity behavior of PANI.

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**CONFLICT OF INTERESTS**

The authors declare that there is no conflict of interests.

**AUTHOR CONTRIBUTIONS**

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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